SEASONAL EXTREMES IN MELTWATER CHEMISTRY AT BRATINA ISLAND (ANTARCTICA):

Physical & Biogeochemical Drivers

Of Compositional Change

A thesis submitted in partial fulfilment of the requirements for the

Degree

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by Briar R. Wait

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For my wonderful family
Michael, Maddison, Kever & Heather
xxxx

And my amazing, super supportive parents
Barbara & Alistair
xx

Abstract

In order to understand and predict the geochemical conditions in Antarctic meltwater ponds during winter, the geochemical extremes in Bratina Island meltwater ponds over a seasonal cycle were determined and compositional variation related to key physical, chemical and biological processes.

A high resolution record of vertical temperature gradients in Skua Pond during freezing, winter and thaw, highlighted a significant seasonal temperature variation (10.3˚C to -41.8˚C) driven by air temperatures and the release of latent heat of fusion. A conceptual model of freeze-thaw involved heterogeneous melting, and explained how the presence of an ice plug near the base of the pond supports the strong chemical stratification observed, which can persist throughout summer.

The geochemistry of Bratina Island meltwater ponds was shown to be catchment specific with correlation between geochemical parameters within ponds, but not between ponds. Basal brines that develop during freezing were nearer in composition to the brines preserved during summer, than to those present immediately post-melting. This is due to mineral precipitation during winter removing selected dissolved ions. Therefore winter brine predictions should be based on mid-late summer conditions, and allow for existing geochemical stratification. Nutrient concentrations were vertically stratified, by the same physical processes controlling major ion concentrations. However, the relatively low nutrient concentrations meant that biological processes exerted little influence over winter brine geochemistry.

FREZCHEM62 modeled winter brine compositions were consistent with those of brines present during progressive freezing. Predicted mineral precipitation was also consistent with the presence of halite (NaCl), mirabilite ($Na_2SO_4.10H_2O$), thenardite (Na_2SO_4), magnesite ($MgCO_3$), gypsum ($CaSO_4$), sodium carbonate ($NaCO_3$) and calcite ($CaCO_3$) in pond sediments. FREZCHEM62 can therefore be used with confidence to predict winter conditions, as long as a reliable initial bulk pond water composition is calculated, and limitations, such as the over-prediction of carbonate mineral formation, are borne in mind.

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Abbreviations

AAS	Atomic Absorption Spectrometer
ARA	Acetylene Reducing Activity
AWS	Automatic Weather Station
DIC	Dissolved Inorganic Carbon
DIN	Dissolved Inorganic Nitrogen
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
DON	Dissolved Organic Nitrogen
DOP	Dissolved Organic Phosphorus
DRP	Dissolved Reactive Phosphorus
EC	Electrical Conductivity
EF	Enrichment Factor
HPIC	High Pressure Ion Chromatograph
MDV's	McMurdo Dry Valleys
MIS	McMurdo Ice Shelf
mS cm^{-1}	milli-Siemens per centimetre
NIWA	National Institute of Water and Atmosphere
PAR	Photosynthetically Available Radiation
SGGES	School of Geography, Geology and Environmental Science
TDC	Total Dissolved Carbon
TDN	Total Dissolved Nitrogen
TDP	Total Dissolved Phosphorus
TDS	Total Dissolved Solids

CHAPTER 1

INTRODUCTION

Figure 1. Field campsite on Bratina Island overlooking tidal lagoon ponds and the Royal Society Range (January 2007).

1.1 Antarctica - a continent for global science

Antarctica is the coldest, windiest, driest and highest continent on Earth; extreme cold has shaped the landscape and the ecosystems living within it. Since the early 19th Century scientific expeditions of Scott, Amundsen, Shackleton and Mawson, the value of science in Antarctica has been recognised (Fogg 1992). Research undertaken in Antarctica has now become fundamental for understanding global processes (Huskies *et al.* 2006) and is an essential component of many scientific disciplines (Walton 2005). More recently, Antarctica is being used as a natural laboratory, as small global changes in climate can have a significant and measurable impact on the polar environment (Huskies *et al.* 2006).

1.2 Inland Waters of Antarctica

Inland waters in Antarctica are unique in that the ecosystems are relatively undisturbed (Huiskes *et al.* 2006) and simple (Vincent *et al.* 2008) compared to similar ecosystems in other parts of the world; consequently, these environments are ideal for ecosystems research. Being an extreme environment, Antarctica offers an insight into ecosystems functioning near the extreme limits of life and it is increasingly recognised that ecological processes are more complex and varied than previously thought (Howard-Williams & Hawes 2007). This provides a unique opportunity to study and create models of ecosystem functioning that, in theory, may be applied to more complex systems elsewhere on Earth (Smith 1985) and potentially extend to include other planets (Marion & Kargel 2008).

Aquatic environments in Antarctica are highly varied in size, depth, temperature, biota and chemical composition. They range in size from large sub-glacial lakes, such as Lake Vostok, which is at least 240 km in length and 50 km in width (Siegert *et al.* 2001); to supra-glacial cryoconite holes just 5 cm in diameter (Fountain *et al.* 2004). Within this broad spectrum are permanently ice-covered lakes such as those found in the McMurdo Dry Valleys (MDV's), pro-glacial lakes, rivers, streams and meltwater ponds. Despite only 2% of Antarctica being ice-free (Lyons *et al.* 2006), it is these areas that host the majority of micro-organisms (Vincent 1987). In these "ice-free" terrestrial ecosystems, solar radiation, temperature and moisture availability are the driving forces behind most biogeochemical processes (Huiskes *et al.* 2006).

Inland waters are ultimately climate-driven as climate determines the hydrological regime within each catchment area (Howard-Williams & Hawes 2007). Therefore, inland waters are highly sensitive to climate change as small changes in temperature around 0°C will determine the presence of liquid water or ice; which will have a significant impact on the environments ability to

support life. Already the importance of this can be seen in the Arctic where events such as the break up of the Ward Ice Shelf (Mueller *et al.* 2003) suggest that global warming is already limiting the occurrence of these inland water ecosystems in the northern hemisphere by reducing the area of ice shelf on which they can occur (Zakhia *et al.* 2008). Consequently, ecosystem research also provides information for the future management of Antarctica's natural resources, and provides baseline information that will allow changes in the ecosystem to be recognised.

Cyanobacteria are the dominant form of life in Antarctic inland waters and layered cyanobacteria mats seen today are similar to those in fossilised stromatolites found in geologic units that are billions of years old (Howard-Williams & Hawes 2007). Howard-Williams and Hawes (2007) note that "the oldest forms of life on Earth, in the oldest known community structure, remain amongst the only ones capable of bringing life to inland parts of Antarctica". Consequently, research on Antarctica's inland waters may also provide a window into the early ecosystems on Earth.

1.2.1 Meltwater Ponds

Meltwater ponds are ubiquitous in Antarctica and are the most common inland aquatic habitat. They are small terrestrial/non-marine water bodies, typically less than 4 m deep and ranging in surface area from a 1 m^2 (de Mora *et al.* 1994) to 30 000 m^2 (Howard-Williams *et al.* 1989) and are found in both coastal and inland environments. They form in the depressions on undulating ice-free ground as a result of basal ice melting and/or snow melt, and show a diverse range of physical and geochemical properties. Examples of abundant meltwater pond areas can be found on the McMurdo Ice Shelf (MIS), Antarctic Peninsula, MDV's, Larsemann Hills, Vestfold Hills, Cape Hallett, Signy Island, La Gorce Mountains, northern Victoria Land and in the Schirmacher Oasis (Howard-Williams & Hawes 2007) as shown in Figure 1.1.

Meltwater ponds in Antarctica are chemically diverse with no single universally applicable process controlling meltwater pond evolution (Webster *et al.* 1994). Instead, meltwater pond composition may be the result of one or several of the following processes:

- Freeze concentration (Wharton *et al.* 1987; Schmidt *et al.* 1991; de Mora *et al.* 1994; Webster *et al.* 1994; Healy *et al.* 2006; Wait *et al.* 2006);
- Ice ablation and summer evaporation (Green *et al.* 1988; de Mora *et al.* 1994; Webster *et al.* 1994);
- Atmospherically transported aerosols (de Mora *et al.* 1994; Hall & Wolff 1998);

- Intrusion of seawater through tide cracks or from seawater trapped in the underlying ice shelf (de Mora *et al.* 1994);
- Groundwater flow (Wilson 1979; Cartwright & Harris 1981), and snow and permafrost melt (Whitehead 1989);
- Chemical weathering of the local geology (Webster *et al.* 1994; Healy *et al.* 2006) and leaching of soil salts (Keys 1980; Webster *et al.* 1994);
- Mineral precipitation (Keys 1980; Cragin *et al.* 1986; Schmidt *et al.* 1991; de Mora *et al.* 1994; Wait *et al.* 2006); and
- Biotic processes (e.g. Vincent & Howard-Williams 1994; Mountfort *et al.* 2003; McKnight *et al.* 2004).

The differing concentrations of major ions and nutrients in meltwater ponds are indicative of solute sources and variation has been noted between ponds of sea- or glacial-water origin (e.g. Cragin *et al.* 1986; de Mora *et al.* 1994; Downes *et al.* 1986; Kerminen *et al.* 2000; Lyons *et al.* 2005; Matsubaya *et al.* 1979; Morrow *et al.* 1962; Webster & Gogual 1988; Webster *et al.* 1994). Increased distance from the sea corresponds with a decrease in the concentration of airborne salt particles (Hall & Wolff 1998); consequently, salt accumulation is partially a function of wind direction and site characteristics such as topography, orientation and precipitation. Accordingly, soluble ionic impurities in Antarctica's coastal meltwater ponds are primarily marine derived aerosols (Whitehead 1989), while meltwater composition in inland areas more closely reflects the weathering products and soil development within the region (Webster *et al.* 1994; Healy *et al.* 2006). Ionic ratios in coastal snowfall show a resemblance to those of seawater suggesting an additional salt precipitation pathway (Whitehead 1989).

One of the most significant processes occurring in meltwater ponds is the annual cycle of freeze and thaw. Unlike many of the large inland lakes in Antarctica, most meltwater ponds freeze solid during winter due to their inability to store heat, which puts considerable stress on the organisms living within these environments (Hawes *et al.* 1999). However, during summer months, fully melted ponds provide relatively warm, nutrient-rich conditions for micro-organism growth (Hawes *et al.* 1993) and liquid water for the dissolution of salts from the soil. This seasonal variation has a big impact on the geochemical properties of the ponds (Wait *et al.* 2006).

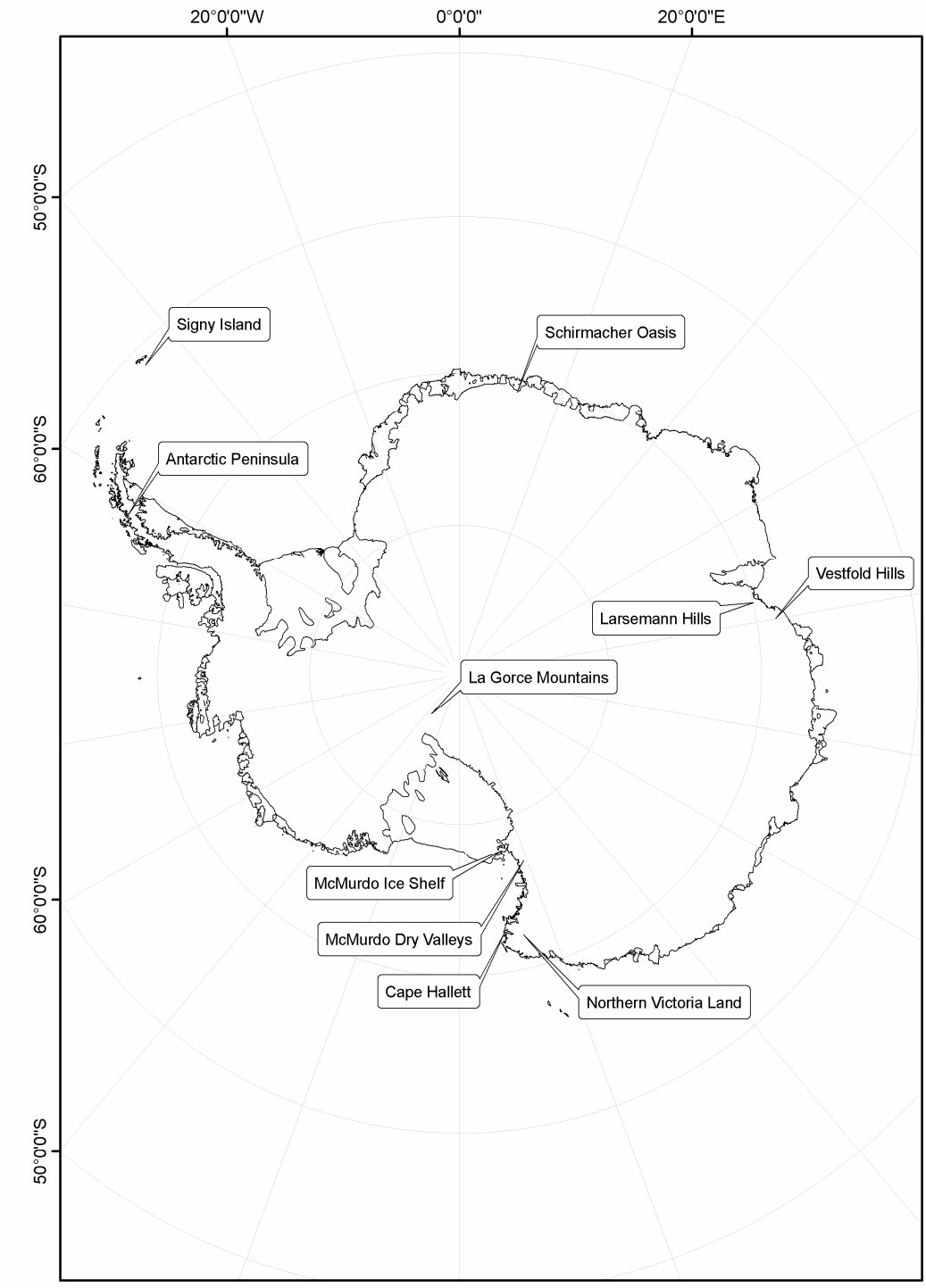

Figure 1.1 Map of the Antarctic continent showing areas of abundant meltwater ponds.

At the end of each summer season, meltwater ponds freeze from the top down in response to a drop in air temperature and a decline in solar radiation. During the winter months, the meltwater ponds are predominantly frozen, however as salts in the pond water are mostly excluded from the

ice, brines may develop at the base of the ponds (Healy *et al.* 2006; Wait *et al.* 2006). These brines are extremely concentrated saline solutions that remain liquid even at very low temperatures (e.g. -18°C) indicating freezing point depression. A good example of this is Don Juan Pond in the Wright Valley. This pond is hypersaline (TDS > 500 kg m^{-3}), precipitating the mineral Antarcticite ($CaCl_2.6H_2O$) (Torri & Osaka 1965), and as a result of freezing point depression does not freeze despite air temperatures as low as -50°C. As ice-covered ponds can not be sampled easily during winter, information on winter conditions predominately comes from the preservation of chemical profiles observed in frozen ponds in late October and in the ponds after melting (Healy *et al.* 2006; Wait *et al.* 2006).

Ponds retaining chemical and thermal stratification were first reported by Schmidt *et al.* (1991) from Ross Island, and Webster *et al* (1994) from the Victoria Valley. It was recognised that the stratification was a result of the pond waters failing to mix during summer melting, with the dense, saline brine formed during winter remaining at the base of the pond. Samples collected only from the top of such ponds (e.g. Whitehead 1989; Timperley 1997) are therefore not representative of whole pond chemistry. Two recent studies of pond stratification; Wait *et al.* (2006) and Healy *et al.* (2006) at Bratina Island on the MIS (78˚S) and in the Wright and Victoria Valleys of the McMurdo Oasis (77˚S) respectively, have confirmed the abundance of stratified ponds and a wide range of mineralogy in salt precipitates. It was also noted in these studies that the process of salt exclusion during freezing is not as complete as had previously been assumed (Wait *et al.* 2006).

1.2.2 Biological Communities within Meltwater Ponds

Meltwater ponds host communities of cyanobacterial mats capable of surviving the extremes of salinity (Schmidt *et al.* 1991), seasonal radiation, desiccation (Hawes *et al.* 1992), and low temperature that prevail in this unique Antarctic environment. Genetic adaptation to growth at low temperatures (psychrophily) is surprisingly uncommon in Antarctic environments and most cyanobacteria, although capable of growth at low temperatures, have optimum growth at warmer temperatures (psychrotrophy) (Vincent 1987). This results in slow growth over time, however, the absence of large herbivores and detritivores enables a significant biomass to be maintained (Howard-Williams *et al.* 1989).

In order to survive Antarctica's extremes, cyanobacteria have evolved several adaptive strategies. In particular, cyanobacteria create their own micro-environment by forming layered mat communities that provides protection from environmental stressors. Mats vary in colour,

thickness and abundance between ponds, but are dominated by the *Oscillatoriacaea* genera (Vincent *et al.* 1993). Colonies of the nitrogen-fixing cyanobacterium *Nostoc* are also common (Quesada & Fernandez-Valiente 2000). The mat provides a semi-permeable membrane between the water and sediment allowing diffusion gradients of dissolved ions, including inorganic carbon and nutrients, to be established. The muco-polysaccharide mat matrix may also inhibit the formation of damaging ice crystals and help to resist desiccation (Howard-Williams *et al.* 2000).

Vertical differentiation occurs within cyanobacterial mats to create sub micro-environments with conditions suited to different cell types. The surface layer is typically orange and carotenoid-rich while the lower layer is often green and phycobiliprotein-rich (Vincent *et al.* 1993a; Vincent *et al.* 1993b). The pigment characteristics (orange in the upper layer and green in lower layer) are a response to light intensity in particular the absolute photon flux density (Quesada & Vincent 1993). Carotenoids in the upper layer screen the high-energy ultra violet (UV), photosynthetically available radiation (PAR) and blue-light wavelengths, changing the spectral light quality and intensity through the mat profile effectively protecting the lower mat layers. The lower layer is supersaturated in oxygen and has high concentrations of both ammonium and dissolved reactive phosphorus (DRP) that are formed by the mat (Quesada & Vincent 1993). The phycobiliproteins capture light energy which is then used for photosynthesis. Additionally, filaments living in the lower layers of the mat are able to quickly (i.e. within 2 hours) migrate to the mat surface if radiation decreases (Vincent *et al.* 1993a; Vincent *et al.* 1993b) allowing cells to take full advantage of optimum light and nutrient conditions.

Overall, the long-term maintenance of cyanobacterial communities in Antarctic meltwater ponds is reliant on maximum growth during the short summer period when light is at its maximum (Hawes *et al.* 1999). However, de-oxygenation, reducing pH and hydrogen sulfide (H_2S) production also indicate that respiratory activities continue well into winter months (Schmidt *et al.* 1991).

1.3 Research Rationale

Meltwater ponds are ubiquitous in many areas of Antarctica (Figure 1.1) and are an essential component of the Antarctic inland waters system. Significant research has been undertaken on the biological aspects of cyanobacterial communities in Antarctic meltwater ponds, yet much remains unknown about the physical and chemical processes operating within this environment, processes which define the geochemical conditions of the biological habitat. Little is known about the seasonal extremes in meltwater ponds, particularly in relation to the geochemical conditions experienced by microbes during winter. Additionally, most Antarctic meltwater pond research

(biological and geochemical) is based on observations of relatively benign summer conditions (Howard-Williams *et al.* 1989; Suren 1990; Hawes *et al.* 1993; James *et al.* 1995) due to the logistical difficulties associated with fieldwork between March and October.

The recognition of chemically stratified water columns in meltwater ponds (Schmidt *et al.* 1991; Webster *et al.* 1994; Healy *et al.* 2006; Wait *et al.* 2006) has had significant implications for our understanding of the tolerances of microbial communities. At different water depths in stratified ponds, microbial communities may be exposed to significantly different chemical and thermal conditions, with the basal brine being the more extreme sub-environment within the pond. When more is known about the processes driving the geochemical development of meltwater ponds, in particular the brine at the base of stratified ponds during both summer and winter, the full extent of microbial tolerances can be quantified. Computer modelling and simulation of freezing processes have the potential to offer useful insights into the geochemical processes operating within meltwater ponds beyond the summer period when geochemical conditions are most extreme. However, confidence in such models is currently limited by a lack of validation in the Antarctic environment.

Understanding the relationship between the geochemistry of meltwater ponds and biological communities may offer new insight into the linkages between the chemistry of major ions and nutrients in this environment. For example, more knowledge of the degree of exchange between inorganic and organic phases of both carbon and nitrogen would have considerable implications for our understanding of nutrient cycling, microbial access to nutrients, and potentially to the way these meltwater systems are modelled.

Bratina Island on the MIS is surrounded by abundant meltwater water ponds that show a diverse range of biological and geochemical features. It is an area that has been the focus of numerous biological studies spanning several decades (e.g. de Mora *et al.* 1994; Hawes *et al.* 1992/1993/1997; Howard-Williams 1986), and to a lesser extent geochemical research (e.g. Hawes *et al.* 1997; Keys & Williams 1981; Whitehead 1989; Wait *et al.* 2006). Significantly, the recent identification of chemical stratification in Bratina Island ponds (Wait *et al.* 2006) presents a unique opportunity to investigate the physical, geochemical and biological factors that may be causing the compositional variation in the water column of meltwater ponds in this area. In particularly, there is potential to look into the relatively unstudied winter environment.

The rationale for continued research in the ponds surrounding Bratina Island is two-fold; firstly to make linkages with previous biological and geochemical investigations in order to better understand the overlap between the two disciplines, and secondly for logistical reasons. Bratina

Island is easily accessible from Scott Base during the summer season and so the timing and specific location of repeat observations can be determined enabling seasonal variation to be accounted for.

1.4 Research Aims & Objectives

The aim of this research is to determine the geochemical extremes in Antarctic meltwater ponds at Bratina Island over a seasonal cycle, and to relate seasonal compositional variations to physical, chemical and biological processes operating within the ponds in order to better understand and predict the geochemistry of meltwater ponds during winter.

This aim is addressed through four main objectives:

1) To fully characterise the seasonal variation that occurs in meltwater pond temperature profiles and relate this to changes in pond geochemistry, such that extreme winter geochemical conditions can be predicted. This will include:
   a. Identification of the thermal gradients that are present in a meltwater pond during a complete freeze-thaw cycle in order to develop a conceptual model of that process; and
   b. Identification of the seasonal geochemical changes in meltwater ponds that correlate with thermal changes occurring at the same time.
2) Characterisation of the spatial and temporal geochemical variation in Bratina Island meltwater ponds. This will include:
   a. Investigating meltwater pond chemistry in a variety of ponds at different stages of freeze and thaw;
   b. Calculation of bulk chemistry to enable direct comparisons to be made between the composition of ponds,
   c. Identification of salt precipitates in and around meltwater ponds; and
   d. Discussion of the factors causing the geochemical variation that occurs in Bratina Island meltwater ponds.
3) To validate the geochemical model FREZCHEM62 (Marion & Grant 1994) developed by the US military for work in permafrost terrain for application in Antarctic meltwater ponds, to enable winter saline brine chemistry to be modelled from either summer basal brine compositions or bulk pond chemistry. This will include:

a. Using FREZCHEM62 to predict evolution of meltwater pond chemistry under both freezing and evaporation regimes;

b. Comparing modelled results with observed chemical evolution of meltwater ponds sampled during the freezing period;

c. Presenting a reliable model for the prediction of winter brine conditions in Bratina Island ponds from summer pond water chemistry.

4) To investigate the relationship between major ions and the inorganic and organic forms of nitrogen, phosphorus, carbon and sulfate in meltwater ponds and to assess the influence of biological processes on winter brine chemistry. This will include:

a. Identification of concentration profiles for nitrogen, phosphorus, carbon and sulfate with depth in meltwater ponds;

b. Identification of physical, chemical and biotic factors influencing the distribution of these ions in the water column;

c. Assessment of the relative importance of biological interaction on the major ion chemistry of meltwater ponds; and

d. Identification of factors controlling redox conditions in meltwater ponds and their brines.

The intent of this thesis is to characterise the geochemical properties of Bratina Island meltwater pond environments in such a way that it improves our understanding of the biogeochemical processes that operate there, particularly during the extreme winter season when field research is limited. This research will improve prediction of winter chemical conditions and provide a context for much of the biological research being undertaken on microbial communities living in meltwater ponds at Bratina Island, making a useful contribution to our general knowledge of ecosystems processes operating in the unique Antarctic environment.

1.5 Thesis Structure

This thesis is divided into seven chapters of which four specifically relate to the primary objectives of this research. These four chapters, Chapters 3, 4, 5 and 6, are intended to be almost "stand-alone" and include a review of the relevant literature, and results and discussion pertinent to each objective. However, the methodology has been separated into Chapter 2 to avoid overlap between chapters and for ease of reference for the reader. Each consecutive chapter builds on the ideas presented in those prior, and these linkages are summarised in the conclusions at the end of each chapter and at the end of the thesis.

1.5.1 Overview of Chapter Content

- Chapter 2 - Research Methodology

This chapter describes all field, laboratory and modelling methodologies used during the course of this research. The field methodology includes site selection, with a description of the field area, as well as sampling techniques and measurement of *in situ* field parameters. Methods used for laboratory analysis of major ion, nutrient and salt content of the water and soil samples are described, as are the geochemical models FREZCHEM62 and PHREEQC that were used to predict equilibrium chemical conditions.

- Chapter 3 – Freeze-Thaw Dynamics & Implications for Stratification & Brine Geochemistry in Meltwater Ponds

This chapter investigates the variation in water column temperature that occurs seasonally within meltwater ponds, and the implications that this temperature variation has for meltwater pond geochemistry. A heat budget and a one-dimensional diffusion model are used to investigate the link between air and water column temperatures and a conceptual model of the freeze-thaw process is presented. These are used to interpret seasonal changes in Antarctic meltwater pond geochemistry and the implication these changes may have on microbial communities.

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- Chapter 4 – Major Ion Behaviour in the Meltwater Pond Environment

This chapter investigates spatial and temporal variation in the chemical composition of Bratina Island meltwater ponds at different stages of freeze and thaw. Meltwater pond compositions early in the melt period are compared to compositions later in the summer season. In addition, repeated sampling of the residual water phase beneath growing surface ice allows changes in the major ion composition of the ponds during progressive freezing to be determined. This chapter also investigates salt precipitation within and around the ponds. Factors that cause the geochemical variation, such as the freeze-thaw process, catchment morphology, stratification, mineral precipitation and redox conditions in Bratina Island meltwater ponds are discussed.

- Chapter 5 – Simulating Major Ion Processes in the Meltwater Pond Environment

In this chapter, the geochemical model FREZCHEM62 is used to simulate the geochemical processes that occur during freezing and evaporation in meltwater ponds. It investigates salt precipitation predicted to occur within the ponds during freezing and evaporation and compares modelled results with salts collected during field sampling. Predicted freeze concentrated brine compositions are compared with water samples collected at various stages of freeze and thaw and the validity of using geochemical models to predict chemical conditions during winter, based on summer water samples, is assessed.

- Chapter 6 - The Effects of Biota on Major Ion Chemistry in Meltwater Ponds

This chapter examines the biogeochemical cycling that takes place in meltwater ponds. In particular it focuses on the relationship between inorganic and organic forms of nitrogen, carbon, phosphorus and sulfate, as well as the redox conditions within the ponds. This chapter uses the conceptual model of freeze-thaw presented in Chapter 3, together with a review of the biogeochemical processes that can effect nutrient concentrations, to determine the influence biota may have on winter brine predictions.

- Chapter 7 – Research Outcomes & Contributions

The final chapter is a synthesis of key ideas that have been put forward in this thesis and of the conclusions made in Chapters 3, 4, 5 and 6. It refers back to the original aims and objectives of this research and makes suggestions for future investigations.

CHAPTER 2

RESEARCH METHODOLOGY

Figure 2. The tide crack, which acts as a hinge between the MIS and Bratina Island, at full melt in January 2007.

This Chapter describes the field site selected for this research and describes in detail the methodologies used throughout this thesis (Chapters 3, 4, 5 and 6 of this thesis only briefly list the methodology used and refer the reader back to this Chapter for further details).

2.1 Site Selection

2.1.1 Bratina Island, Antarctica

The MIS is a 1500 km^2 ablation zone at the northwest extent of the Ross Ice Shelf, between Ross Island and Brown Peninsular (Mountfort, *et al.* 2003; Vincent *et al.* 1994). The area consists of moraine covered ice formed by basal freezing of seawater and the upward migration of marine sediments as a result of ablation. The area has an undulating, irregular surface topography with a vertical profile of up to 20m (Howard-Williams *et al.* 1989) and between 10% and 60% of the ice shelf is covered with meltwater ponds, stream and lakes (Vincent et al. 1994).

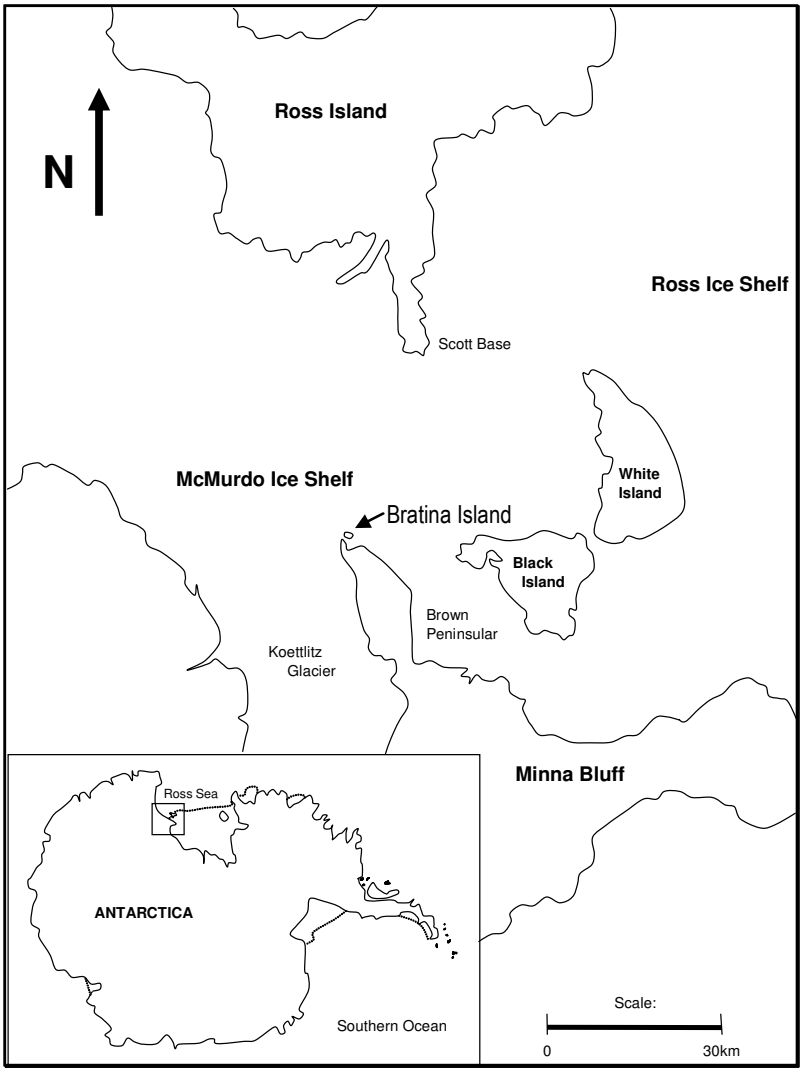

Figure 2.1 Map showing the location of Bratina Island on the MIS approximately 35 km southwest of Scott Base on Ross Island in Antarctica (inset).

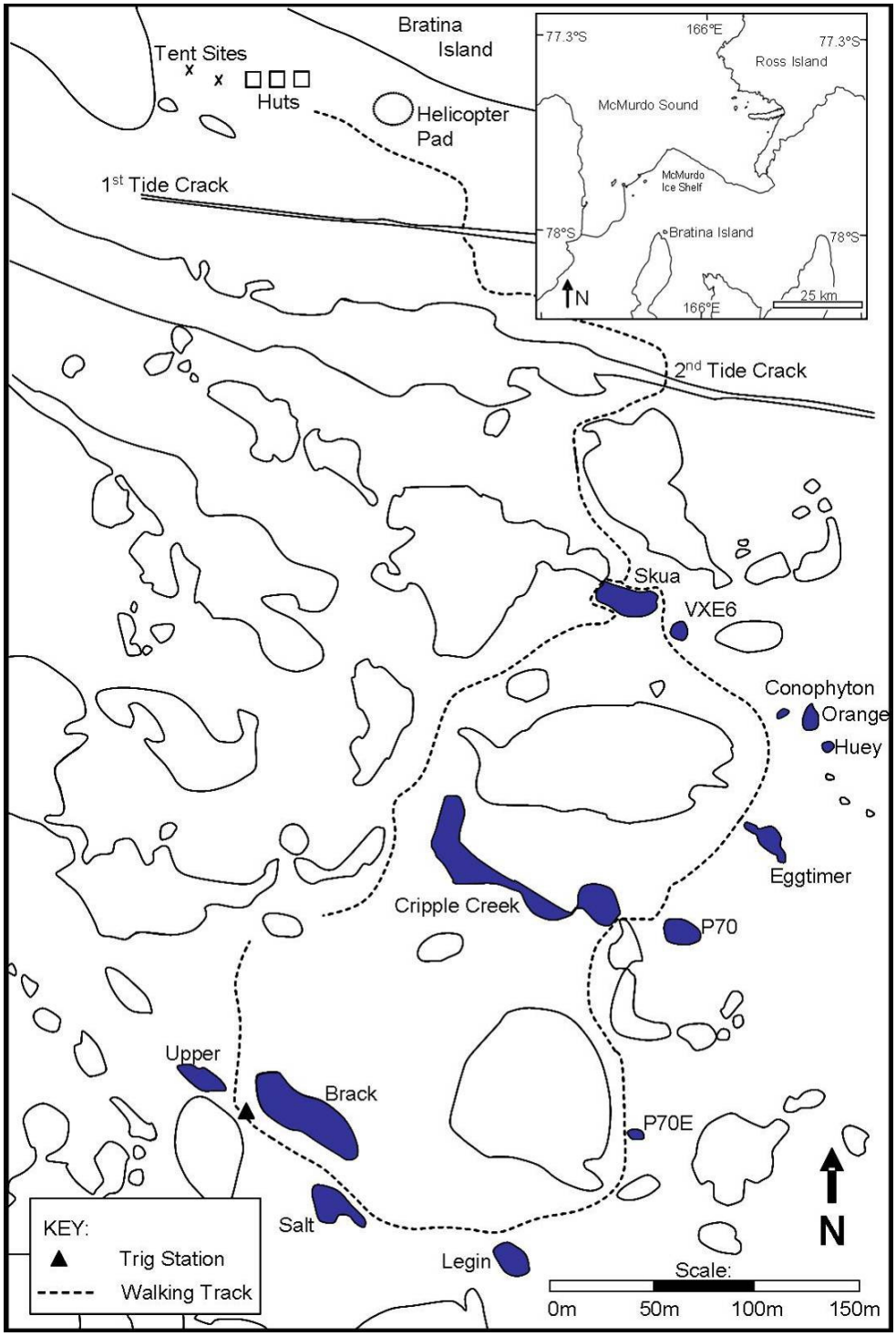

Figure 2.2 Locality map for Bratina Island, Antarctica (inset) and the 13 meltwater ponds used in this study (shaded) (modified from Wait *et al.* 2006).

Bratina Island (165°30'W, 78°00'S) is a volcanic cone situated within the MIS near the tip of Brown Peninsula, approximately 35km southwest of Scott Base. The ice shelf directly surrounding Bratina Island comprises numerous isolated meltwater ponds and has been the

primary research site for the NIWA "Antarctic Aquatic Ecosystems" research project for several decades. It was also the site used by Wait *et al.* (2006) in an earlier study of meltwater pond geochemistry that provided some of the background data for this research. Good background information, including meteorology, was available for this site and it was relatively accessible from Scott Base, with a permanent field camp that could be revisited each summer season. Therefore the MIS surrounding Bratina Island was selected as the principle field site for this thesis. Figure 2.1 shows the location of Bratina Island on the MIS and Figure 2.2 identifies the meltwater ponds included in this study. For ease of reference and consistency with previous work, the ponds in this study will be referred to as "Bratina Island ponds", despite the fact that they occur on the MIS immediately adjacent to the island and not on the island itself.

2.1.2 Bratina Island 05/06

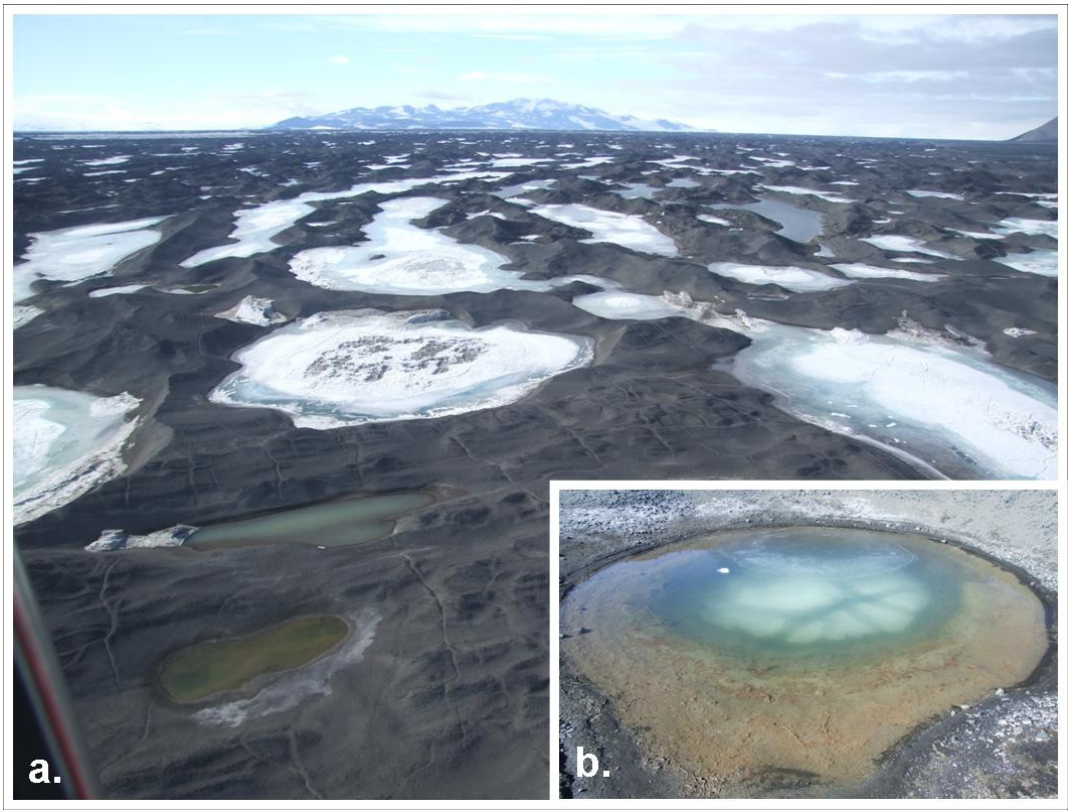

Figure 2.3 a. View of the MIS adjacent to Bratina Island in December 2005, when the majority of meltwater ponds had significant ice cover; b. An intact, subsurface ice plug in VXE6 pond.

A total of ten days was spent at Bratina Island for the period 19th to the 28th of December 2005. On arrival in the field the majority of meltwater ponds had significant ice cover (i.e. >80% ice) and only very small and/or saline ponds were fully melted out (Figure 2.3a). This limited the meltwater ponds that could be selected for this study to relatively small (most <3.5m in diameter) ponds. The presence of ice plugging the base of many meltwater ponds (Figure 2.3b) also prevented the

measurement of fully melted pond profiles, however their presence allowed for an improved understanding of the freeze-thaw process in meltwater ponds as discussed in Chapter 3.

2.1.3 Bratina Island 06/07

A total of 14 days were spent at Bratina Island between 16th January and 29th January 2007. This coincided with the mid-summer melt period when the meltwater ponds had undergone maximum melting and had not yet begun to refreeze. The vast majority of ponds were fully melted (Figure 2.4), with the exception of some large, fresh, 'permanent' ice ponds. All study ponds sampled in the 05/06 season were still present and were all ice free.

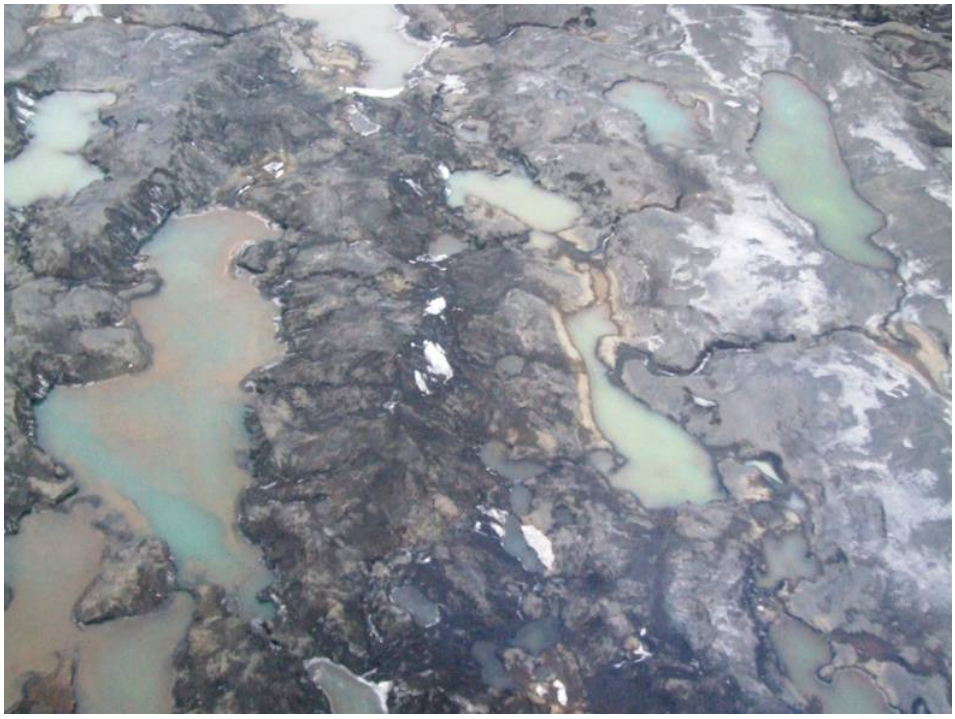

Figure 2.4 View of the MIS adjacent to Bratina Island in January 2007, when the majority of meltwater ponds were fully melted.

2.1.4 Bratina Island 08

A special extended field season as part of the International Polar Year allowed field work to be undertaken at Bratina Island between late January and April 2008. This fieldwork was completed by Ian Hawes and Karl Safi from NIWA with samples being made available to this study. Initially the majority of ponds were fully melted enabling observations to be made and samples to be collected as freezing commenced in early to mid February. By the end of this field season, all ponds had 100% ice cover and contained a significant volume of ice; however the ponds were not completely frozen to the base of the water column as will be discussed.

2.2 Field Methodology

In order to standardise the position of measurements taken at different depths at different time periods in meltwater ponds, measurements are referred to as a height above sediment rather than a pond depth per se. For example, this means that water taken from the base of a pond is recorded as 10 cm above the sediment and water from the surface of a pond is a higher value such as 100 cm above the sediment. This allows samples to be compared between seasons even if water levels have changed significantly.

Additionally, a distinction can be made between a "surface sample" and a "surface layer". A surface sample refers to water collected from approximately the top 10 cm of the water column, usually from near the edge of a pond, whereas the surface layer of a pond refers to the upper mixed portion of a stratified water column that can be sampled from any number of depths, depending on the physical and chemical structure of the pond, and give the same result.

2.2.1 Pond Temperature Logging 2005

Figure 2.5 An 8 string thermistor chain was deployed in the centre of Skua Pond between 27 February to 18 December 2005, to measure water temperature at heights of 10, 20, 40, 60, 80, and 100 cm above the base of the pond. Air temperature was also measured 120 and 140 cm above the base of the pond.

On 27 February 2005, an eight string thermistor chain was deployed in the centre of Skua Pond, to measure water temperature at heights of 10, 20, 40, 60, 80, and 100 cm above the base of the pond (the maximum pond depth was approximately 110cm when fully melted) (Figure 2.5). Air temperature was also measured 120 and 140 cm above the base of the pond. Deployment was

organised by Jenny Webster-Brown at the University of Auckland and instigated by Ian Hawes and Donna Sutherland of NIWA. Campbell CS107 temperature probes recorded data onto a Campbell CR10 datalogger at hourly intervals from 27 February 2005, then three hourly from 2 April 2005 to 1 October 2005, and then hourly again until the download of data on 18 December 2005. Data was downloaded by NIWA staff and then made it available for use in this study.

2.2.2 Meltwater Pond Sampling

The first stage of fieldwork in 05/06 and 06/07 was to measure conductivity profiles in a wide variety of ponds along the established walking route (Figure 2.2) to identify those with stratification. Based on the criteria that they were fully melted and showed conductivity stratification four meltwater ponds; P70, P70E, Upper and Huey, were selected as principle study ponds (Figure 2.6). These four ponds were photographed, the major dimensions were measured, and the following sampling procedure was undertaken.

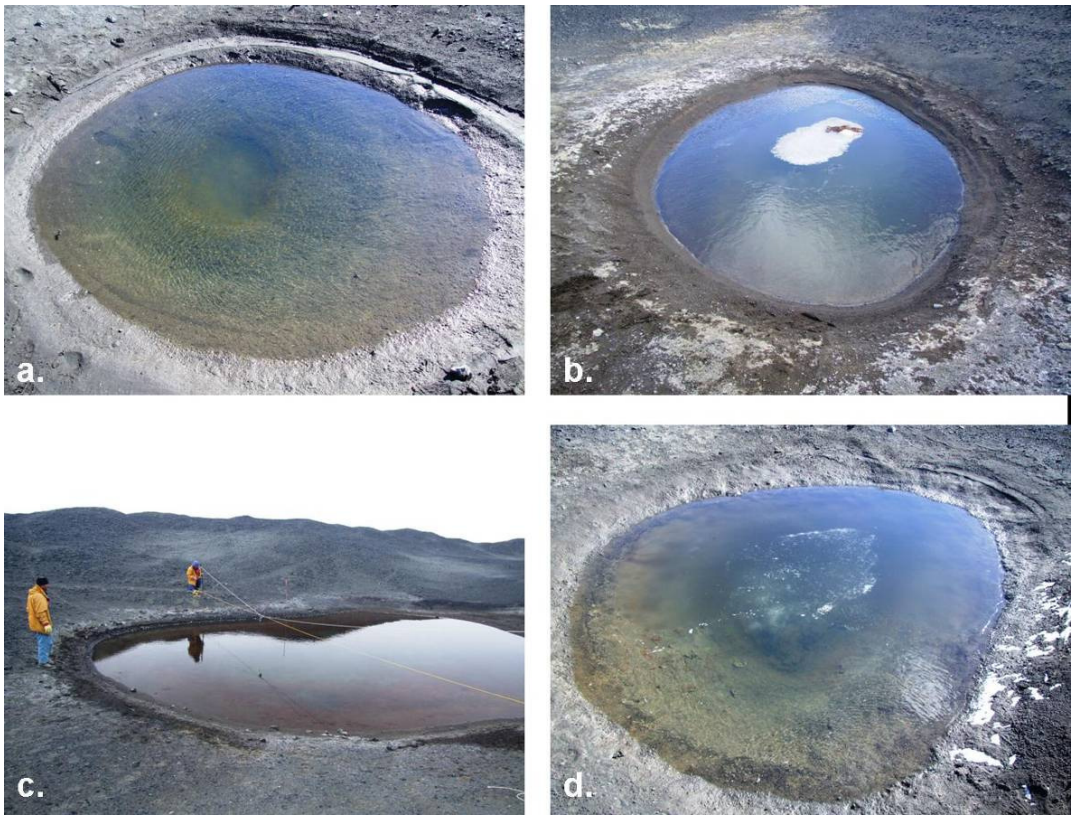

Figure 2.6 Four of the principle study ponds (a.) P70E Pond (b.) Upper Pond with floating ice (c.) P70 Pond (also Ian Hawes and Brian Sorrell) (d.) Huey Pond with intact subsurface ice. All photographs taken in December 2005.

Two methods were employed to access water samples from different depths at the centre of each meltwater pond; a “fishing pole” method used for small ponds (Figure 2.7), and a “pulley system” method used for small-medium sized ponds (Figure 2.8). These methods were used for both *in*

situ measurement of physical parameters (Section 2.2.3) and for water sample collection (Section 2.2.4).

Figure 2.7 Pond sampling method using bamboo "fishing pole" technique to access water samples from the centre of small meltwater ponds. This photograph shows Briar Wait (left) and Brian Sorrell (right) sampling P70E Pond in December 2005.

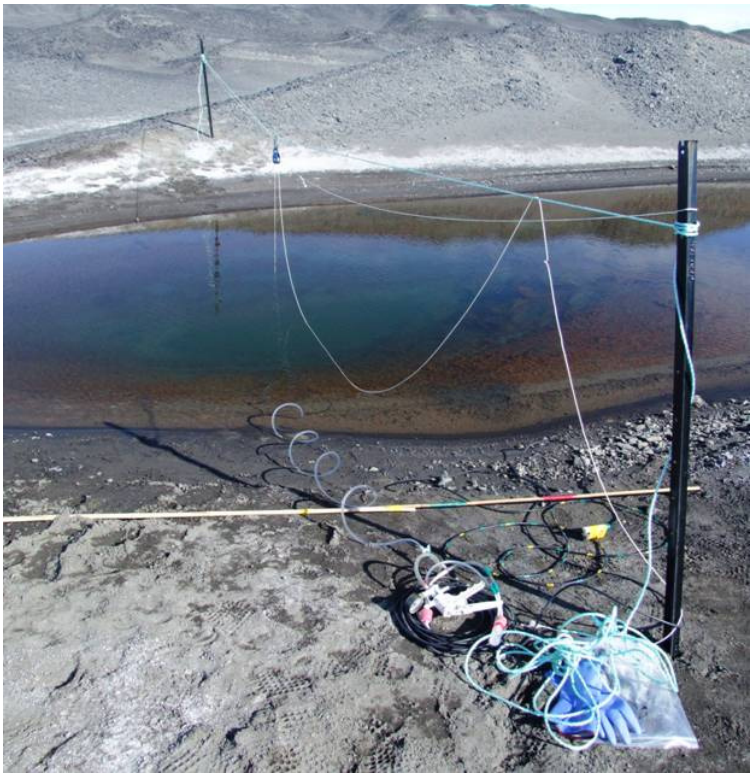

Figure 2.8 Pond sampling method using waratahs and rope, and a pulley system to access water samples from the centre of small-medium sized ponds – in this case Eggtimer Pond in January 2007.

2.2.3 *In situ* Field Measurement of Physical Parameters

In situ profiles of redox potential, temperature, conductivity, and pH were taken in the deepest part of the meltwater ponds selected in the initial pond survey. Measurements were recorded at 5 cm to 10 cm depth intervals, starting at the surface of the pond, with additional measurements taken at the very base of the pond as required. Redox potential (Eh) was measured using a platinum wire electrode referenced against an Ag/AgCl electrode and read using a volt meter. Temperature, conductivity, pH and dissolved oxygen were measured using standard portable field meters. The pH meter was calibrated using a 3 point calibration against pH buffers of 4.0, 7.0 and 10.0 (at approximately field temperatures), prior to sampling and soaked in distilled water between uses. The probe was rinsed with distilled water between ponds and with pond water between consecutive samples. The conductivity meter was calibrated prior to field work commenced and the DO meter was calibrated against $NaSO_3$.

2.2.4 Water Sample Collection and Preservation Procedures

Table 2.1 Preservation and storage procedure for each water quality sampling parameter.

Sampling Parameter	Sample Volume	Preservation & Storage Procedure
Dissolved Organic Carbon	1 x 50ml	Sample filtered through a glass microfibre filter (Whatman GF/F) and stored in an autoclaved Schott bottle (glass). Filters were ashed at 500°C to remove carbon residue prior to filtering. A tin foil cover was put over the neck of bottle to reduce chance of carbon contamination from bottle lid. Samples were stored in a refrigerator.
Nutrients	1 x 100ml	Sample filtered through a glass microfibre filter (Whatman GF/F) and stored in an acid washed bottle. Samples were frozen until analysis.
Hydrogen Sulfide	1 x 50ml	Unfiltered samples were collected with minimal aeration and little air inclusion and preserved immediately with 5 drops of 1M Zn zinc acetate solution. Samples were stored in a refrigerator.
Bicarbonate	1 x 50ml	Sample bottle filled to maximum capacity with unfiltered sample to avoid air bubbles. Stored in a refrigerator.
Major Ions	2 x 50ml	Unfiltered samples were stored in a refrigerator.

Depending on the size of the pond, the fishing pole or the rope and pulley system was set up over each study pond for the duration of sampling as shown in Figure 2.7 and Figure 2.8. This allowed a slow smooth lowering of the sampler and an accurate, repeatable depth measurement. Both methods required a hand vacuum pump and plastic tubing to extract water samples which were pumped directly into clean sampling tubes. The shortest length of tubing needed to access the base of the pond was used to minimise the volume of water extracted from each pond. Based on the *in situ* conductivity profiling, various depths were identified for sampling that were representative of the stratified layers.

The tubing used for sampling was flushed with the volume of pond water equivalent to the tubing volume and then, using a hand vacuum pump, samples were collected from each depth into the appropriate sample bottle (either a sterile 50ml centrifuge tube, a 100ml acid washed polypropylene bottle, or a autoclaved 50ml schott bottle depending on the parameter being measured). The temperature, pH, conductivity, dissolved oxygen concentration and redox potential were immediately measured (using the same methods described above) in a small volume of sample from each sample depth, which was then discarded.

Samples were collected, preserved and stored using the methods given in Table 2.1.

2.2.5 Sediment Sampling Procedure

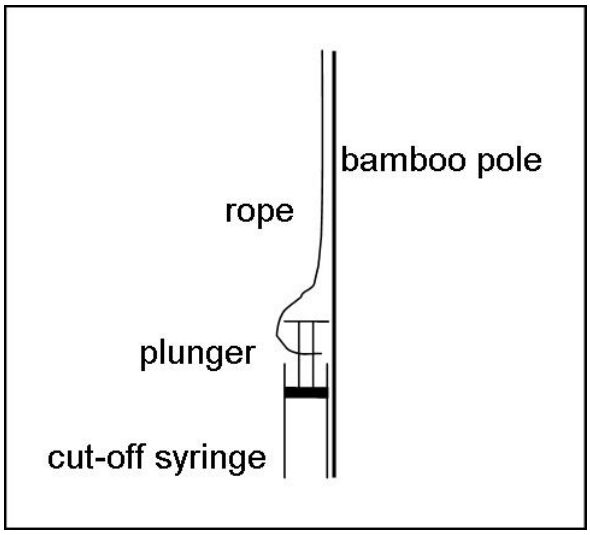

Figure 2. 9 Sediment corer devised from a cut-off 50 ml syringe (27 mm in diameter) attached to a bamboo pole with rope to pull plunger when inserted into pond sediment.

If salt precipitates were present around the margins of the pond, samples of these were collected using a spatula into a 100ml sediment container. Sediment cores were collected from within the meltwater ponds by pulling the plunger up on a cut-off 50 ml syringe, attached to a bamboo pole,

as illustrated in Figure 2.9. Upon extraction of the core a second plunger was inserted into the open end of the syringe to hold the core in place. Cores were then stored in the dark in an upright position until frozen.

Sediment cores were typically 3 – 5 cm in length and topped by cyanobacterial mat. The success of core extraction was dependant on the coherency of the substrate and the size of the sediment material. Sediment material sand-sized or smaller (i.e. < 2 mm) produced the longest cores while granule and pebble-sized material (i.e. > 2 mm) generally could not be sampled.

2.2.6 SIPRE Ice Coring

In order to collect an ice core from Skua Pond, the centre of the pond was drilled with a covax drill to estimate pond depth. A SIPRE ice auger, shown in Figure 2.10, was then used to collect ice core which was broken off at 10 - 20cm intervals and bagged for transportation back to the field camp where the ice was melted into 500ml Nalgene bottles. The basal brine was sampled using a hand vacuum pump and a length of tubing.

Figure 2.10 Collecting an ice cores using the SIPRE ice auger (October 2001).

2.3 Analytical Methods

All major ion concentrations were analysed as mg kg^{-1} with measurements being made by weight as opposed to volume. Nutrient concentrations were measured by volume and are presented as mg (or µg) L^{-1}, which is approximately equal to mg (or µg) kg^{-1} in all but the most saline samples where the water density is >1 g L^{-1}.

2.3.1 Bicarbonate (HCO_3)

Titration was used to determine the concentration of HCO_3 in meltwater pond samples. Samples remained sealed and refrigerated until analysis could take place, and in all cases titrations were

completed within 4 weeks of sample collection. Using pH as an indicator, samples were titrated against standardised HCl (0.01 mol kg^{-1} for sample conductivities < 7.5 mS cm^{-1} and 0.1 mol kg^{-1} for sample conductivities > 7.5 mS cm^{-1}) from pH 8.3 to pH 3.8. If the initial sample pH was >8.3, HCl was added to ensure that all CO_3^{2-} in the sample was present as HCO_3^-. Back titration against NaOH (0.01 mol kg^{-1} for sample conductivities < 7.5 mS cm^{-1} and 0.1 mol kg^{-1} for sample conductivities > 7.5 mS cm^{-1} prepared daily from 1 M CO_2-free stock solution stored under N_2) eliminated possible interference by other ions (such as borates and phosphates) that may contribute to alkalinity (as per Wait *et al.* 2006). The HCO_3 concentration was then determined from the difference (concentration and volume) between the two titrations, divided by the sample volume (10ml).

2.3.2 Hydrogen Sulfide (H_2S) Analysis

The standard methylene-blue colorimetric method (APHA, 1998) was used to determine total sulfide in the meltwater samples. This method is based on the reaction of sulfide, ferric chloride, and dimethyl-p-phenylenediamine to produce methylene blue. Ammonium phosphate was added after colour development to remove ferric chloride colour. To ensure low H_2S concentrations were detected, samples were pre-concentrated by weight (samples were weighed, allowed to settle, then the decant was poured off before being reweighed). The detection limit (after pre-concentration of the samples) was 0.005 mg kg^{-1} with a precision of approximately 0.001 mg kg^{-1}.

2.3.3 Major Ions (Na, K, Mg, Ca, Cl and SO_4)

Major ion analysis took place in the water quality laboratory at the School of Geography and Environmental Science, University of Auckland. Samples with a high concentration of major ions were diluted prior to analysis using serial dilution by weight with ultrapure water. Dilutions ranged from 0 (raw sample) to a maximum dilution of 1770 times for water collected from the base of Eggtimer Pond. A GBC Avanta Atomic Absorption spectrometer (AAS) was used to analyse the major cations, Na, K, Mg and Ca, in each water sample. Sodium was added to K, Mg and Ca standards for ionization suppression. Limits of detection for cations were 0.4 mg kg^{-1} for Na, 1 mg kg^{-1} for K, 0.4 mg kg^{-1} for Mg and 1 mg kg^{-1} for Ca. High Pressure Ion Chromatography (HPIC) was used to measure major anion concentrations, SO_4 and Cl, in the meltwater samples using a Dionex IC-2000 HPIC with an ASRS Ultra II 2mm column. The eluent (10mM NaOH) and the reagent (10mM H_2SO_4) were pumped at a flow rate of 1ml/min. Methods for HPIC were based on those by Webster *et al.* (1994), Welsh *et al.* (1996), Healy *et al.* (2006) and Wait *et al.* (2006) who successfully used ion chromatography to analyse waters from Antarctic waters.

Quality Control

Standards were run in triplicate at the beginning of each day for both HPIC and AAS and the median result used for deriving calibration equations. Standard were also repeated at the end of each day to detect any drift that may occur. The expected standard deviation and error in the samples was determined by running a single sample 10 times. The standard deviation of the duplicates was <1 % for both cations and anions. Ion balances (APHA, 1998) were calculated for each sample as an internal quality control check, as well as select replicate analyses. The ion balance was <5 % in the majority of samples and all were <10%.

A Mohr titration was used to determine the concentration of Cl in a selection of meltwater pond samples as a quality control check for Cl concentration results obtained by HPIC. A 0.1 mol L^{-1} silver nitrate solution was prepared from solid $AgNO_3$ (that had been dried for 2 hours at 100°C and allowed to cool) and ultrapure water. A 0.25 mol L^{-1} potassium chromate indicator solution was also prepared. A burette containing silver nitrate solution was set up (on a stand) over a 250 ml conical flask containing a 10 ml aliquot of sample was diluted with 50 ml of distilled water and 1 ml of chromate indicator. The sample was then titrated with 0.1 mol L^{-1} silver nitrate solution, the end point being the first appearance of the red-brown colour of silver chromate. Titrations were repeated in triplicate for each sample.

Good agreement was observed between HPIC and $AgNO_3$ titration results indicating that the large dilution required for some samples for HPIC analysis did not affect the accuracy of results. Dilutions of up to 1:6000 have yielded good results (standard deviations <1%) for water samples analysed by HPIC collected from the MDV's, Antarctica (Welch *et al.* 1996).

2.3.4 Nutrients

Nutrient samples collected and filtered in the field were analysed for nitrate (NO_3-N), ammonia (NH_4-N), total dissolved nitrogen (TDN), total dissolved phosphorus (TDP), dissolved reactive phosphorus (DRP) and organic carbon (DOC). Samples were analysed by High Pressure Liquid Chromatography (HPLC) in the chemistry laboratory at NIWA (Hamilton) by NIWA technicians. The dissolved organic phosphorus (DOP) and dissolved organic nitrogen (DON) were calculated by difference as shown in Equation 2.1 and 2.2 below:

$$\mathbf{DOP = TDP - TRP} \qquad \textbf{Equation 2. 1}$$

$$\mathbf{DON = TDN - (NO_3\text{-}N + NH_4\text{-}N)} \qquad \textbf{Equation 2. 2}$$

2.3.5 Sediment Analysis

Frozen sediment cores were sectioned in half lengthways using a clean band saw while still in the modified syringe. One half of each core was returned to the freezer while the other half was air-dried. Sub-samples of soils and salts were taken from the air-dried samples for salt identification using a scanning electron microscope (SEM) in the Engineering School at the University of Auckland. The SEM used was a Philips XL30S FEG (FEG = Field Emission Gun) with a SiLi (Lithium drifted) EDS detector. Salts were mounted on small Al stubs and sputter coated with Pt prior to SEM analysis.

2.4 Geochemical Modelling

2.4.1 FREZCHEM62

FREZCHEM62 (Marion *et al.* 1994) is an equilibrium chemical thermodynamic model that can model progressive freezing and evaporation, chemical fractionation and equilibrium crystallisation. It models aqueous solutions with high ionic strengths (i.e. up to 20M) across a range of temperatures (+25°C to -60°C) at atmospheric pressure, making it particularly suitable for modelling the meltwater pond environment. The FREZCHEM62 model utilises Pitzer equations to calculate activity coefficients and the activity of water. The model includes solubility products for fifty solid phases, principally Cl, SO_4, NO_3 and HCO_3-CO_3 bearing minerals and ice, and is based on the Gitterman model of the chemical freezing pathway (Marion 1999).

Inputs to the FREZCHEM62 model include the concentrations of Na, K, Ca, Mg, Cl and SO_4, initial pH, carbonate alkalinity (in this case the concentration of HCO_3 in equivalents kg^{-1}) and atmospheric CO_2. A choice can be made in FREZCHEM62 to model using either equilibrium or fractional crystallisation. For the purposes of this research, equilibrium crystallisation offered better representation of the meltwater environment, as minerals predicted to precipitate are retained in the system and continue to interact with the residual fluid. The FREZCHEM62 model can be run to model both freezing and evaporation. Under the freezing regime, the initial and final temperature for the modelling and the required temperature decrement in Kelvin units are input to the model before the data is converged. Under the evaporation regime, the initial and final weight of water (1000 g reducing to 10 g) and the water increment (10 g) are input to the model before the data is converged.

Determining Model Inputs – Calculating Bulk Pond Chemistry

As meltwater ponds are commonly stratified, a bulk composition of each pond needed to be determined in order to input an initial concentration for each parameter into the FREZCHEM62

model. A method used by Canfield and Green (1985) was adopted and modified to suit the meltwater pond environment. By using the dimensions of selected ponds (width across two main axis and depth) and by assuming that the ponds are cone-shaped, a total volume of each pond can be calculated. By maintaining the ratio of pond depth to pond radius the volume of smaller cones within each pond can be determined enabling the volume of each chemically diverse layer to be derived. Using the compositions and volume of each stratified layer for the study ponds in December 2005 and January 2007, the total concentration of major ions in each stratified layer was calculated and the bulk chemistry of each pond determined. Once the input data had been entered into the FREZCHEM62 model, small discrepancies in the ion balance were corrected by altering the Cl concentration (in all cases this alteration was less than a 10% change to the Cl concentration). The same method was used to determine the bulk pond composition of ponds sampled repeatedly in 2008 with the residual brine volume and % ice volume being calculated for each sampling period.

2.4.2 PHREEQC

PHREEQC is an equilibrium geochemical model that simulates low temperature chemical reactions and transport processes in natural (and polluted) waters (Parkhurst & Appelo 1999). In this study the most recent available version of PHREEQC was used (version 2, downloaded from the USGS website on the 4th February 2008) along with the thermodynamic data in the MINTEQ v.4 database. PHREEQC was primarily used to determine the redox state for selected meltwaters using the redox pairs S(-2)/S(+6) and O(-2)/O(0). Inputs to the model included the major ion and nutrient composition, water temperature, pH, dissolved oxygen concentration and the electrode potential (pe) of the meltwater solution. The pe of the system is a theoretical measure of the oxidising (positive pe) or reducing (negative pe) intensity of a water body where ae^- is the electron activity (see Equation 2.3), and is related to field measurements of Eh by using Equation 2.4 (where n is the moles of electrons in the defined cell reaction (n = 1, 2, 3 etc), F is the Faraday Constant, R is the universal gas constant and T is absolute temperature).

$$pe = -\log_{10} ae^- \qquad \textbf{Equation 2.3}$$

$$pe = ((nF)Eh)/2.303RT \qquad \textbf{Equation 2.4}$$

It was assumed that the redox state in oxidised meltwater ponds was primarily controlled by oxygen and therefore that n = 2 (see Equation 2.5).

$$\tfrac{1}{2}O_2 + 2H^+ + 2e^- = H_2O \qquad \textbf{Equation 2.5}$$

CHAPTER 3

FREEZE-THAW DYNAMICS AND IMPLICATIONS FOR STRATIFICATION AND BRINE GEOCHEMISTRY IN MELTWATER PONDS

Figure 3. Summer snowfall at the Bratina Island field camp, Antarctica (December 2005).

This Chapter has been published as a journal paper by the title "Freeze-thaw dynamics and the implications for stratification and brine geochemistry in meltwater ponds on the MIS, Antarctica" in Antarctic Science. The lead author was B. Wait (the author of this thesis), and co-authors were R. Nokes (University of Canterbury) and J. Webster-Brown (University of Auckland). The co-authors contribution included the initial idea and equipment to record the temperature variation in Skua Pond (J. Webster-Brown) and the writing of the two mathematical models (R. Nokes). Chemical data collection, analysis and interpretation were undertaken by the author of this thesis.

3.1 Context of this Research

Antarctic meltwater ponds are small inland water bodies that form in the depressions on undulating surfaces as a result of ice and snow melt (de Mora *et al.* 1994). They are ubiquitous on the MIS, covering an area of 1500 km^2, as well as being found in ice-free areas of Antarctica (e.g. Wharton *et al.* 1985, Vincent & Howard-Williams 1986, Howard-Williams at al. 1986, Howard-Williams at al. 1989, Howard-Williams *et al.* 1990, Webster *et al.* 1994; Timperley *et al.* 1997, Healy *et al.* 2006). The meltwater ponds on the MIS host one of the largest concentrations of non-marine organisms in the southern Ross Sea (Hawes *et al.* 1997) and exhibit diverse physical and geochemical environments within and between ponds (Wait *et al.* 2006). Some meltwater ponds in this area are stratified during winter, with chemical and thermal stratification persisting in some ponds through the summer period (Wait *et al.* 2006). Unlike larger Antarctic lake environments, the majority of meltwater ponds freeze solid in winter and fully melt out each summer (Hawes *et al.* 1999) making this a unique environment exhibiting a significant degree of seasonal change.

The temperature of meltwater ponds controls the presence or absence of liquid water (Howard-Williams & Hawes 2007). Consequently, seasonal temperature variation in meltwater ponds, particularly during periods of freeze and thaw, is central to several key physical, biological and geochemical processes. The activity of the microbiological communities that inhabit these ponds also responds to the seasonal cycle of solar radiation and water temperature (Goldman *et al.* 1972, Hawes *et al.* 1993), as temperature plays an important role in the regulation of photosynthesis (Rae *et al.* 2000).

Freeze and thaw of meltwater ponds is a direct response to changes in solar radiation and air temperature (Hawes *et al.* 1997) as in other high latitude water bodies (Cozzetto *et al.* 2006) and cold climate lakes (Kouraev *et al.* 2007). The basic, generally accepted, model of freeze and thaw is as follows: Freezing is initiated at the pond surface in response to a drop in air temperature. Ice grows downward along the temperature gradient between the cold atmosphere and relatively warm basal pond water (Iliescu *et al.* 2002). During the process of freezing, dissolved ions are excluded from the ice and concentrated into the residual water phase eventually forming saline brine with a depressed freezing point (de Mora *et al.* 1994, Marion & Grant 1994, Marion 1997, Wait *et al.* 2006, Healy *et al.* 2006). Pond melting is initiated from the base of the pond as air temperatures and solar radiation increase in early summer (Hawes *et al.* 1999).

This basic model of temperature and chemical change (hereafter referred to as the "Top Down Bottom Up, or "TDBU" model) is consistent with observed meltwater pond behaviour in some cases. For example, migration of the freezing front from the pond surface downwards was observed by Schmidt *et al.* (1991) in meltwater ponds at Cape Evans (Ross Island, Antarctica) during winter freezing and in three ponds on the MIS (Hawes *et al.* 1999). In the later case, downward freezing was attributed to reducing air temperatures and attenuation of incident radiation penetration due to ice cover (Hawes *et al.* 1999).

However, several observations have been reported that suggest a departure from the TDBU model of the freeze-thaw process. Although melting was thought to be initiated at the base of the MIS ponds, it was noted that there was ice remaining at the base of one of the ponds in early summer (Hawes *et al.* 1999). Additionally, imperfect salt exclusion during freezing and the encapsulation of brine inclusions in the ice at the freezing front in MIS ponds resulted in increased conductivity and major ion concentrations with depth in the ice profile (Wait *et al.* 2006).

One of the obstacles to understanding meltwater ponds has been the lack of detailed temperature data over a full annual cycle, particularly data relating to thermal gradients with depth. Consequently, the physical process by which ponds undergo cycles of freezing and melting, and how this may deviate from the TDBU model described above, remains poorly understood. The presence of more complex thermal gradients in summer and winter would make the prediction of winter brine chemistry more difficult, therefore limiting our understanding of ecosystem functioning and the tolerance of biota to winter extremes. Deviation from the TDBU model of pond thaw behaviour during early summer melt is also likely to affect the development and persistence of summer stratification, which again would affect biological processes.

3.1.1 Contribution of this Research

In this study a high resolution record of pond temperature gradients has been collected from Skua Pond, a MIS pond near Bratina Island, over a period of 10 months. For the first time, pond water chemistry has been interpreted in the light of measured seasonal variations in pond temperature and visual observations of the pond during freeze-thaw. The hypothesis was that the thermal gradients developed within meltwater ponds during freeze-thaw differ significantly from those predicted using the accepted, TDBU model of this process. In turn, this will influence the development and persistence of chemical stratification and mineral precipitation with implications for understanding the extreme chemical conditions occurring in meltwater ponds during winter.

3.2 Sampling techniques and analytical methods

The location of Bratina Island (78°S 166°E) and the ponds included in this study are shown in Figure 2.2. On 27 February 2005, eight Campbell Scientific CS107 temperature probes were deployed in the centre of Skua Pond by NIWA staff, to measure water temperature at heights of 10, 20, 40, 60, 80, and 100 cm above the base of the pond (the maximum pond depth was 110 cm when fully melted) and air temperature 120 and 140 cm above the base of the pond. Measurements were recorded onto a Campbell CR10 data logger at hourly intervals from 27 February 2005, then three hourly from 2 April 2005 to 1 October 2005, and then hourly again until the download of data by NIWA staff on 18 December 2005.

Water sampling was undertaken in December 2005, soon after the ponds had melted, and again in late January 2007, when the ponds had been fully melted for some time. In 2005, the 4 study ponds were selected on the basis that they were stratified and fully melted; in 2007 the same 4 ponds were re-sampled along with 3 new ponds. Using portable meters, vertical profiles of conductivity, dissolved oxygen and redox (2007 only) were measured *in situ* at the deepest part of 4 ponds (all stratified) in December 2005 and in 7 ponds (5 stratified and 2 mixed) in January 2007. In December 2005, additional conductivity profiles were taken in 7 ponds that had not completely melted and contained residual ice near the base of the pond. Water samples (60 ml) were also collected from the water column for hydrogen sulfide (H_2S) analysis, and preserved using 1M Zn acetate. The samples were later analysed using the methylene-blue colorimetric method (APHA, 1998).

3.3 Results

3.3.1 Seasonal Temperature Variation

The high resolution record of surface air temperatures and pond temperatures collected from representative water depths in Skua Pond for 294 days during 2005 is shown in Figure 3.1a and b. This record spanned the freezing and thawing period in the pond, with pond temperatures ranging from a high of 10.3°C (measured 10 cm above the base of the pond in late April) to a low of -41.8°C (at the pond surface in mid-August) giving an annual temperature range of 52.1°C within the pond. Air temperatures at the surface of the pond ranged from above 0°C in summer to a winter low of -46.6°C.

Within the pond, strong seasonal cycles were demonstrated as well as temperature fluctuations that occurred over periods of days to weeks, and even distinct diurnal cycles that showed hourly changes (particularly evident in Figures 3.1a and b which provide a magnified record during the

freezing and thawing phases). The significance of seasonal weather patterns were also evident when surface air temperatures increased by approximately 30°C over a period of about 15 days in mid to late June (around 3000 hours on Figure 3.1b).

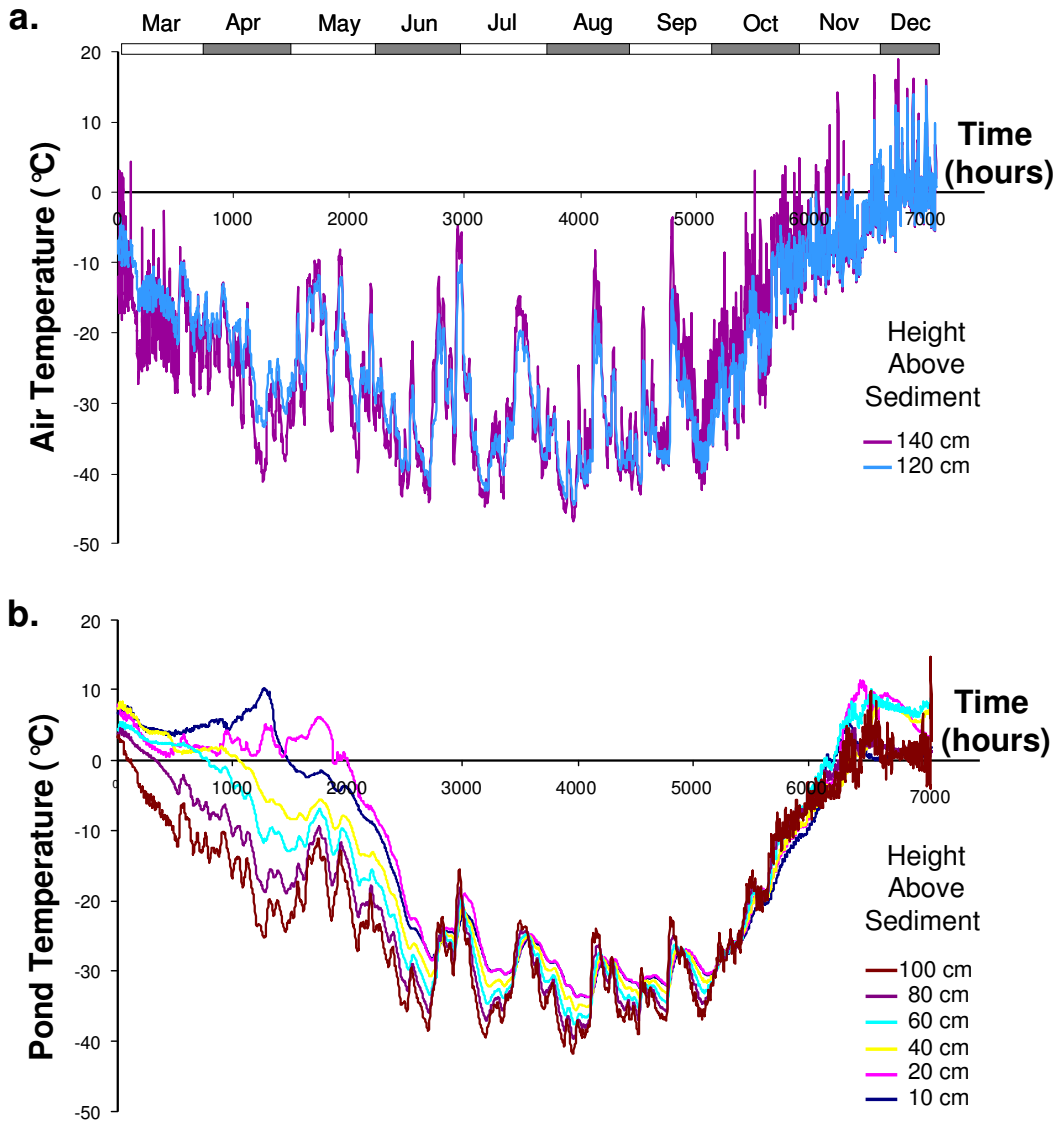

Figure 3.1 (a.) The high resolution record of air temperature recorded 120 cm and 140 cm above the base of Skua Pond from 27th February to 18th December 2005. (b.) The temperatures in the water column measured 10, 20, 40, 60, 80 and 100 cm above the base of Skua Pond for the same period.

During the freezing phase, between late-February and May (0 to 2200 hours, Figure 3.2a), the temperature measured near the bottom of the pond was largely unresponsive to the rapidly dropping temperatures in the surrounding environment. During this time, substantial vertical thermal gradients were evident within the water column. The greatest thermal gradient occurred in late April (1285 hours) with a temperature gradient of approximately 35°C measured through the water column, just before the period of complete darkness set in. For the majority of the year

the surface layer of the pond was considerably colder than the basal layers with the exception of brief periods over winter when the pond exhibited an inverted temperature gradient (e.g. 2975, 3500, 4160 and 4805 hours, Figure 3.1b). In winter, the temperatures in the pond were strongly correlated with those in the air above.

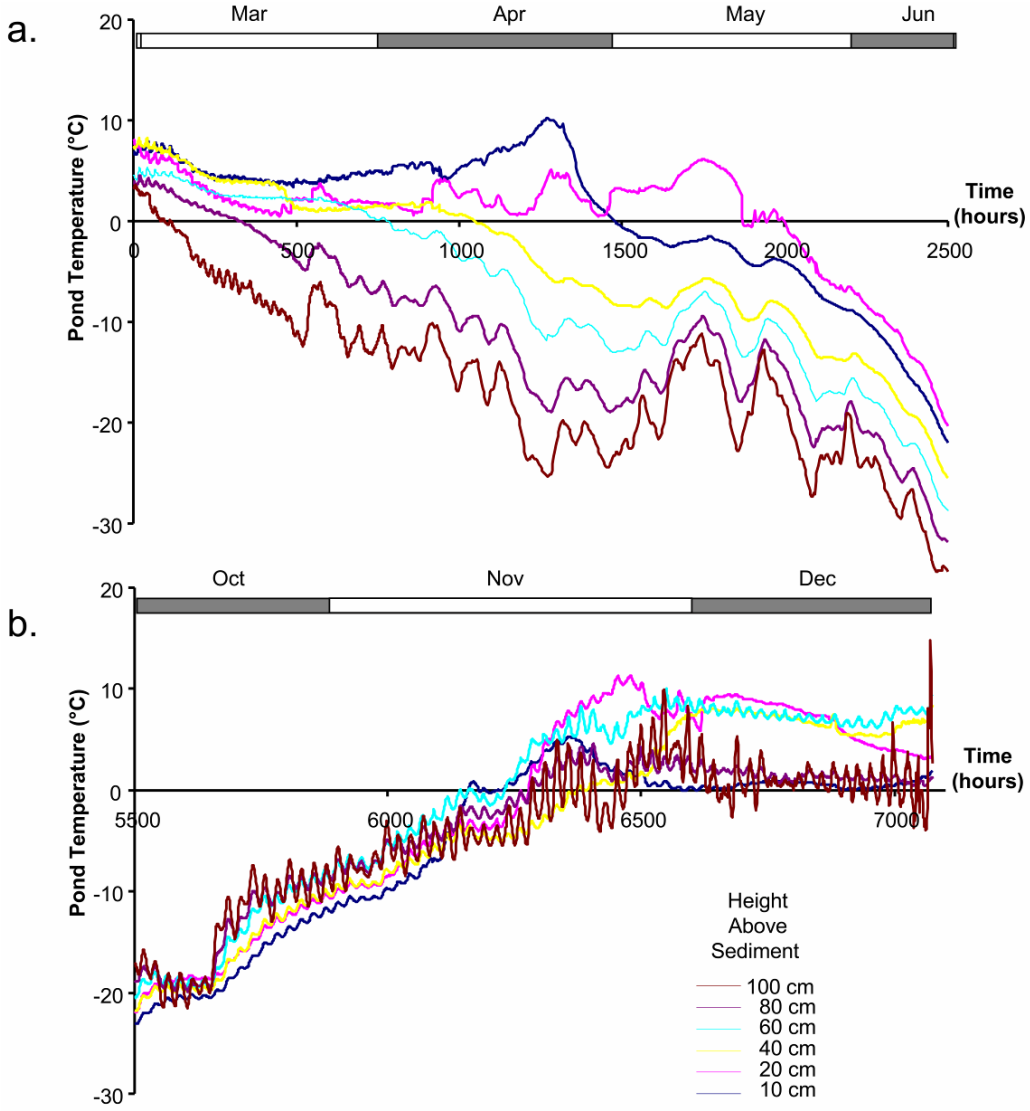

Figure 3.2 The temperature profiles recorded in Skua Pond in 2005 during (a.) freezing (late February – mid June) and (b.) thawing (October – December).

3.3.2 Water Temperatures during Freeze and Thaw

The temperature data collected for the period during which the meltwater pond actively began to freeze (mid-February to May) is shown in Figure 3.2a. During the first 500 hours (up to mid-March), the pond temperature record showed the near surface layers (100 cm and 80 cm above the base of the pond) cooling steadily and falling below 0°C early in this period. Conversely, the water layers 60 cm and below showed only weak cooling and, after approximately 250 hours, the

temperature effectively stabilized well above 0°C. The exception to this behaviour was exhibited by the record 20 cm above the base of the pond, which fluctuated between 0°C and 5°C.

At approximately 570 hours the temperature 10 cm above the base of the pond began to increase from 4.1°C, to a maximum temperature of 10.3°C at approximately 1270 hours (mid to late April). During this 30 day heating period, the temperature at the base of the pond increased by approximately 6°C, at a time when the majority of the pond water was cooling rapidly.

Figure 3.3 Thermistor chain in Skua Pond at time of data download on the 18th December 2005. The pond was 100% ice covered with weak candled ice.

The temperatures recorded at various pond depths during thawing, through September to the end of the record (i.e. from 5500 hours onwards), are shown in Figure 3.2b. The complexity of seasonal temperature change during this time is clearly evident. As observed during freezing, the temperatures at the base of the pond appeared to respond quite differently to the near surface water temperatures. Initially the base of the water column was the coldest layer in the pond but

then warmed rapidly and was the first layer to exceed 0°C (at 6170 hours). For the later half of November, both the surface of the pond and the water column 40 cm above the base of the pond showed the least warming remaining colder than the rest of the pond.

From around 6400 hours (late November) the majority of the ponds water column was >0°C, even though the surface air temperatures remained below freezing point. For most of December, the water column exhibited a temperature maximum varying between 7.5°C and 9.5°C at mid-depths (20 - 60 cm above the base of the pond) with colder layers above and below (generally <2°C). At the time of the data download Skua Pond was observed to be 100% ice covered with weak "candled" ice (thin vertical candle-like ice crystals) as shown in Figure 3.3.

3.3.3 Field Observations of Meltwater Ponds during Thaw (December 2005)

Table 3.1 Conductivity measured in selected ponds containing an intact ice plug on the 21st December 2005. Measurements were taken in situ 10 cm below the pond surface in the centre of the pond (Layer 1), immediately overlying the ice plug in the centre of the pond some distance below the pond surface (Layer 2) and at the contact between the edge of the ice plug and the pond sediment adjacent to the basal brine (Layer 3).

Pond	Conductivity mS cm^{-1}		
	Layer 1	Layer 2	Layer 3
VXE6	2.56	2.65	
Orange	1.13	1.14	1.13
Conophyton	0.412	0.421	
Legin	1.12	1.14	
Cripple Creek	0.404	0.394	
Eggtimer	1.78	2.25	
Huey	2.74	8.02	18.0

In December 2005, the meltwater ponds near Bratina Island were in different stages of melt. Across a small area (Figure 2.2), ponds ranged from being 100% covered in ice, with an unknown ice volume (e.g. Permanent Ice Pond and Duet Pond), to fully melted with 0% ice cover, and no ice volume (e.g. P70E Pond). In Cripple Creek, Skua Pond and Eggtimer Pond (Figure 2.2) surface ice remained in the centre of the pond, with a fully melted moat around the pond edges. In these ponds, the surface ice appeared fixed near the centre of the pond, suggesting that it was

attached in some way to the base of the pond. As melting progressed, the surface ice became free floating allowing it to be blown across the pond surface according to the prevailing wind direction.

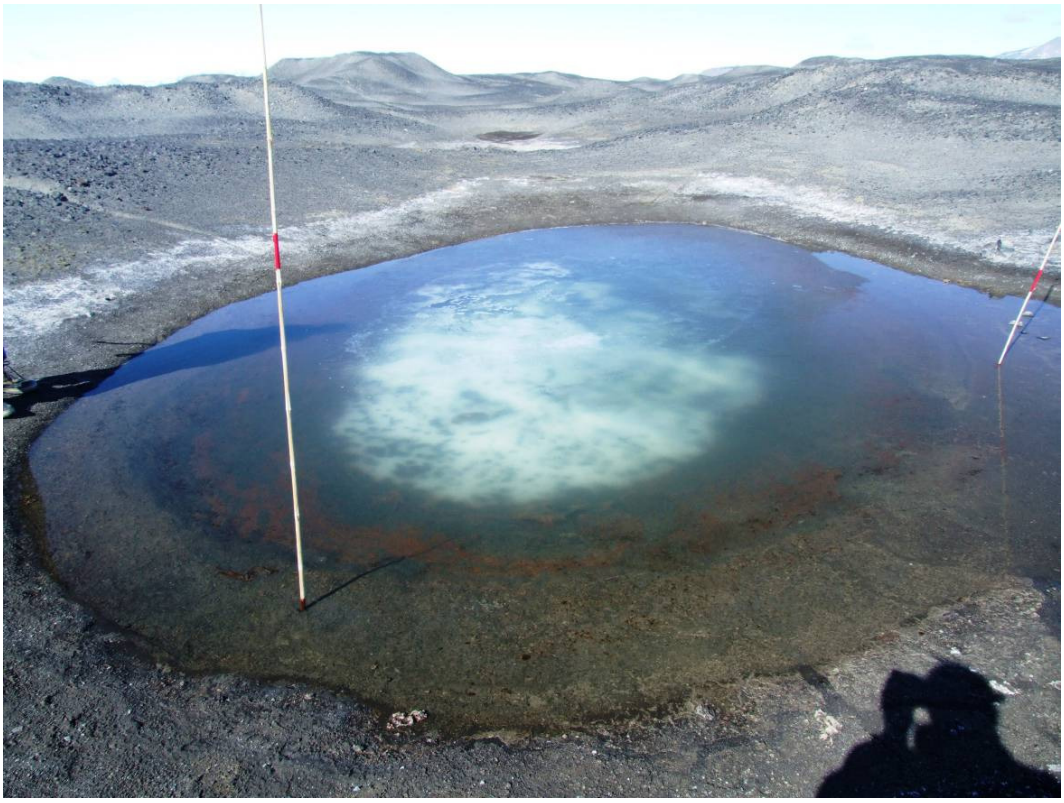

Figure 3.4 Orange Pond with an intact ice-plug near the base of the pond, December 2005.

In many ponds, 7 of which were profiled for conductivity (Table 3.1), a submerged layer of ice occurred approximately 10-40 cm above the base of these ponds during thawing, trapping liquid brine beneath it. This 'ice plug' was frozen in place where the ice made contact with the edge sediments. During the 10 days in the field, the ice plugs gradually melted away from the sides of all but one of these ponds (Orange Pond; Figure 3.4) until it became detached and floated to the pond surface. Once the ice plug was released, the ponds showed visual characteristics of stratification (as noted by Wait *et al.* 2006), such as the greenish viscous appearance of water in the deepest section of the pond (see Figure 3.5).

Figure 3.5 Greenish viscous appearance of summer basal brine in VXE6 Pond, December 2005.

3.3.4 Water Chemistry during the Thaw and Summer Period

In ponds with an intact ice plug (December 2005), the water column overlying the ice was generally well mixed with little or no increase in conductivity adjacent to the ice plug surface (Table 3.1). The exception to this was measured in Huey Pond where the water column showed increased conductivity adjacent to the ice plug due to partial melt of the ice away from the edge sediments and subsequent "leakage" of Layer 3 (Table 3.1) brine. Figure 3.6a shows conductivity profiles in Huey Pond at various stages of melt, illustrating the importance of the ice plug in creating chemical stratification. Once the ice plugs had floated to the surface of the ponds, strong conductivity stratification was evident (e.g. 4.8 mS cm^{-1} at the surface of VXE6 Pond increasing to 75 mS cm^{-1} at the base, see Table 3.2). Table 3.2 summarizes selected geochemical characteristics of the study ponds after full thaw had occurred for 2005 and 2007.

Anoxic conditions and the presence of H_2S at the base of the ponds in December 2005 (refer Table 3.2) showed that the basal brines had been physically and chemically isolated from the fully melted, oxygenated water column above the ice plug. In Huey Pond and Upper Pond basal water samples were taken soon after the ice plug release; concentrations of H_2S were 14.8 mg kg^{-1} and 0.2 mg kg^{-1} respectively and dissolved oxygen concentrations were low but measurable (1.27 mg L^{-1} in Huey Pond and 1.0 mg L^{-1} in Upper Pond). Concentrations of H_2S and DO in Huey Pond are illustrated in Figure 3.7.

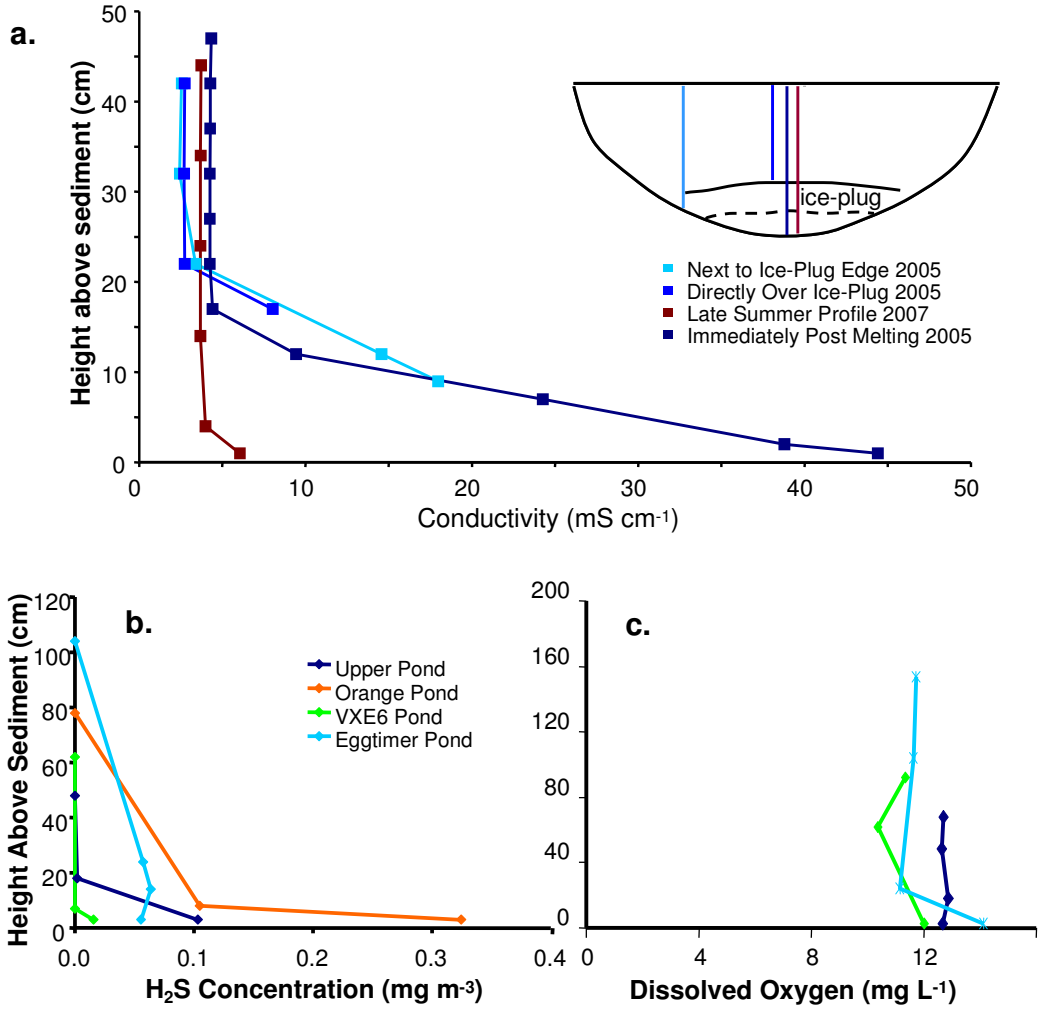

Figure 3.6 (a) Conductivity profiles in the water column of Huey Pond overlying an ice plug, immediately post ice plug melting in mid-summer, and in late-summer. (b) Hydrogen sulfide concentrations in VXE6, Upper, Eggtimer and Orange Pond in late summer 2007 when the ponds were fully melted. (c) Dissolved oxygen concentrations in VXE6, Upper and Eggtimer Pond in late summer 2007 when the ponds were fully melted.

In late January 2007, conductivity stratification was still present in 5 of the 7 study ponds. In the 5 ponds that were profiled in both years, the conductivity and thickness of the brine layer was reduced in 2007 compared to 2005 (with a maximum conductivity of 36.1 mS cm^{-1} compared to 75 mS cm^{-1} and a maximum thickness of 0.17 m compared to 0.32 m in 2007 and 2005 respectively, see Table 3.2). Detectable levels of H_2S (ranging from 0.02 mg kg^{-1} to 0.33 mg kg^{-1}, see Table 3.2) were present in some stratified brines despite their apparent saturation with dissolved oxygen (Figure 3.6b and c). This co-existence of oxygen and H_2S is very unusual and is discussed later in Section 3.4.6.

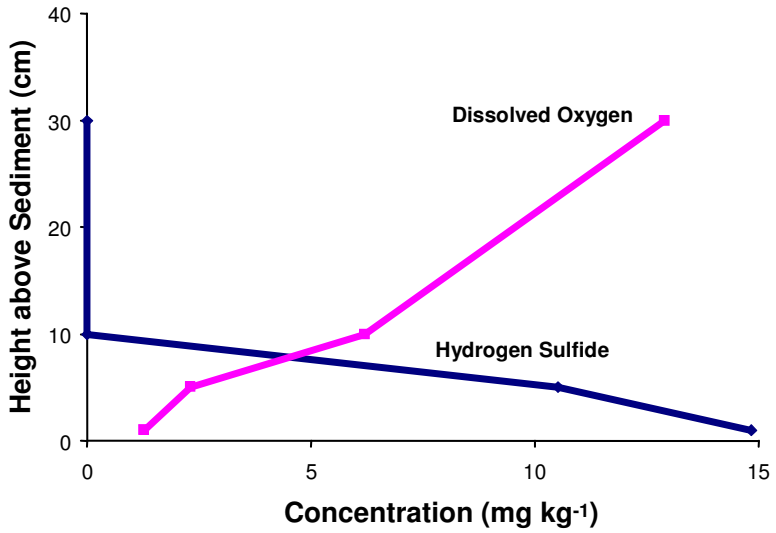

Figure 3.7 Concentrations of H_2S and DO in Huey Pond immediately post ice-plug release in December 2005.

Table 3.2 Selected geochemical properties of the 7 meltwater ponds included in this study measured in December 2005 and late January 2007. The ponds were fully melted at the time of sampling. nd = not detected, nm = not measured, * indicates the pond was not stratified at the time of sampling, and only a single representative sample was taken from the mixed water column.

Pond	Year	Max Depth m	EC surface mS cm^{-1}	EC base mS cm^{-1}	Brine Layer m	H_2S base mg kg^{-1}	dO_2 surface mg L^{-1}	dO_2 base mg L^{-1}	Temp surface °C	Temp Base °C
VXE6	05	0.99	4.8	75	0.24	nm	nm	nm	2.9	-0.3
	07	0.92	5.74	35.2	0.12	0.016	10.4	12.0	4.8	5.8
Huey	05	0.50	4.17	41.8	0.11	14.8	12.9	1.27	9.4	6.9
	07*	0.53	3.68		nd	nd	12.2		7.7	
P70	05	0.96	4.78	74	0.06	nd	12.3	14.5	7.5	6.5
	07	1.09	9.62	9.69	nd	nd	nm	nm	6.5	5.9
P70E	05	0.67	6.17	55	0.3	nd	12.6	20	4	4
	07	0.81	5.66	35.1	0.1	nd	11.4	12.6	8.7	7.2
Upper	05	0.62	7.5	39.3	0.32	0.2	13.9	1.0	4.9	3.8
	07	0.68	4.51	36.1	0.17	0.10	12.6	12.7	4.4	11.5
Orange	07	1.28	2.1	32.2	0.05	0.33	nm	nm	4.2	4.9
Eggtimer	07	1.54	2.5	64.1	0.25	0.056	11.6	14.1	5.4	7.3

3.4 Discussion

3.4.1 Factors Controlling Meltwater Pond Temperatures

Regional climate is the primary influence on changes in pond temperature. Data from the automatic weather station (AWS) Pegasus North (http://amrc.ssec.wisc.edu/aws/archive/Pegasus_Narchive.html 30.05.07) on the McMurdo Ice Self (77.95°S, 166.50°E, 8m elevation), approximately 23 km from Bratina Island, shows that regional air temperature changes coincide with changes in pond temperature in Skua Pond, confirming the dominance of a regional weather effect rather than localized or micro-scale events.

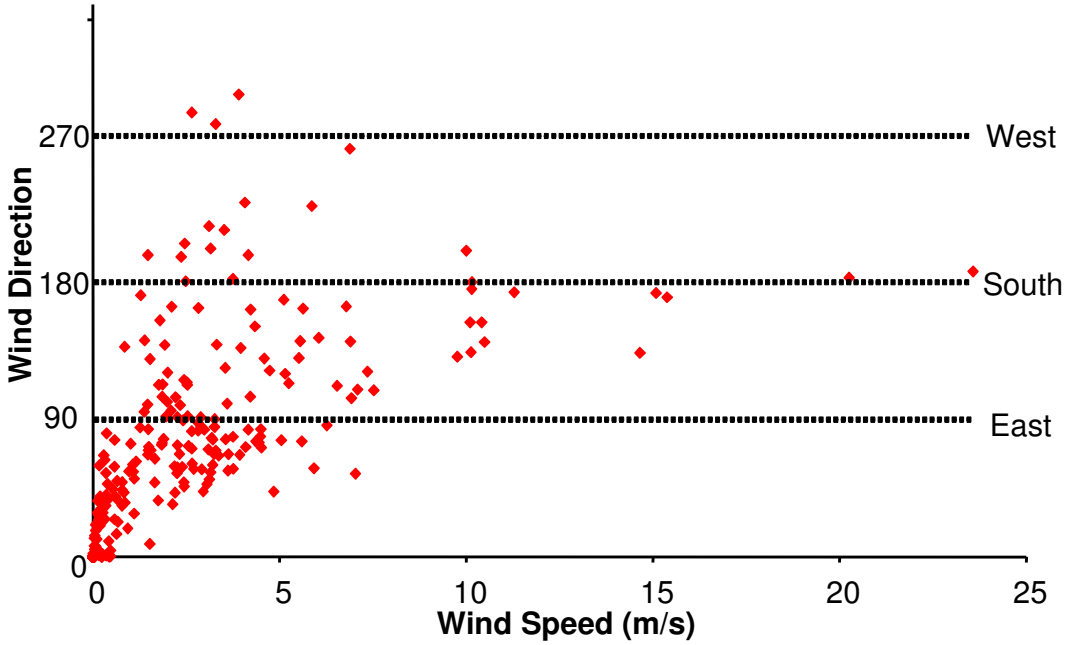

Figure 3.8 A comparison of wind direction with wind speed from the Pegasus North AWS near Bratina Island shows clearly that strong wind events originate from the south.

By comparing wind direction with wind speed in the area near Bratina Island it is apparent that strong winds are predominantly from the south, with lesser winds coming from a primarily north-easterly direction (Figure 3.8). Data from the Pegasus North AWS show that periods of rapid warming coincide with strong (>10 m s^{-1}) wind events, particularly from a Southerly direction (inland) suggesting that warming events are caused by foehn or katabatic winds moving through the region from more elevated inland areas (Nylen *et al.* 2004). These events were particularly apparent in the pond record during winter as they caused pond temperatures to increase by up to 24°C in a single event (e.g. 2975-3205 hours). The rapid response of the surface ice resulted in short periods of normal temperature stratification in the pond. There was evidence of at least 6 of these rapid warming events during winter 2005 (Figure 3.1a and b).

A strong diurnal temperature signal was visible in the pond temperature record during the periods when 24 hour daylight was present (before 500 hours and after 5000 hours in the record). These diurnal changes are related to the change in solar energy flux during the day, with topographical shading and cloud cover potentially contributing to the variation (Vincent 1988). Interestingly, even during periods with only partial darkness (approximately 500 -1500 hours and 3450 to 5000 hours in Figure 3.1b), the solar energy was sufficiently weak that the temperature signal within the pond no longer exhibited a significant diurnal signature. In the absence of a solar energy flux during the complete darkness of winter, variation in pond temperature was governed by air temperature alone.

Pond temperature, driven by air temperature, ultimately controls the freeze and thaw processes and the presence, or absence, of ice at different times of the year. In turn, ice cover affects geochemical and ecosystem processes by influencing mixing, sedimentation and radiative transfer, as well as physiological characteristics of microbial communities (Fritsen & Priscu 1999). Temperature also plays an important role in determining the physical properties of the water within the pond contributing, along with salinity, to the density of water and consequently to convection within a pond. Therefore, pond temperatures play a direct role in determining the presence, or absence, of stratification.

Four distinct phases, representing the seasons, occur annually within meltwater ponds, three of which are illustrated in the temperature record presented here. These four phases consist of a Freezing Phase, a Winter Phase, a Thaw Phase and a Summer Phase (not measured here) all of which show unique temperature variation reflecting the physical processes operating in the pond at that time. Each of these phases has a significant influence on the geochemical processes occurring at that time.

3.4.2 The Freezing Phase

The freezing phase takes place from approximately mid-February to late-May. As temperature and the intensity of solar radiation decrease towards the end of summer, ice begins to form on the surface of the meltwater ponds and freezing commences. An important process that occurs as the meltwater freezes is the release of latent heat, the energy released when water changes state to form ice. The latent heat of fusion influences meltwater pond temperatures, having reportedly caused the delay of microbial mat freezing in high latitude northern hemisphere ponds (Mueller & Vincent 2006). It has also been identified as the additional source of heat at the ice-water interface in mid-latitude ponds (Rogers *et al.* 1995). A slight increase in water temperature,

immediately prior to freezing in several MIS ponds has been previously attributed to the release of latent heat of fusion (Hawes *et al.* 1999).

In order to appreciate the extent to which the latent heat of fusion has contributed to the temperature variation measured during freezing in Skua Pond, a simple heat budget has been calculated. This heat budget considers only the first 1000 hours of the temperature record and makes the following assumptions: Heat transfer in the pond is one-dimensional (heat transfer through the sides of the pond is ignored) and the base of the pond is a no-flux boundary; the heat loss through the pond surface is by diffusion alone and the upper layers of the pond are the first to begin freezing; and the top 60% of the pond is assumed to be frozen by the end of the 1000 hour period as suggested by the temperature record (Figure 3.1b). The physical properties of water and ice are as given in Table 3.3, and the fully melted water depth is taken to be 110 cm.

An estimate of the temperature gradient at the surface of Skua Pond was based on the difference in temperature between the two near surface temperature probes (100 cm and 80 cm above the base of the pond), which varied over the 1000 hour period but averaged around -25 °C m^{-1}. Thus the heat loss through the pond surface is estimated as 60 W m^{-2}, corresponding to a heat loss of 2.2 x 10^8 J m^{-2} over the 1000 hour period.

Table 3.3 Physical properties of water and ice used in the heat budget calculations and mathematical models.

Physical Property	Symbol	Value	Units
Density of water	ρ_w	1000	kg m^{-3}
Density of ice	ρ_i	917	kg m^{-3}
Thermal conductivity of water	k_w	0.55	W $m^{-1}K^{-1}$
Thermal conductivity of ice	k_i	2.4	W $m^{-1}K^{-1}$
Specific heat of water	c_{pw}	4190	J $kg^{-1}K^{-1}$
Specific heat of ice	c_{pi}	1960	J $kg^{-1}K^{-1}$
Latent heat of fusion for water/ice	L	334	kJ kg^{-1}

To determine the heat loss from the residual water phase within Skua Pond as it cooled, approximate values from the temperature record were used. The top 60% of the water column that was assumed to freeze cooled by approximately 5°C in its liquid state, before cooling a further 8°C in its solid state. Therefore the latent heat of fusion released by the upper 60% of the

water column that changes state during the 1000 hour period is 2.2 x 10^8 J m^{-2} (based on the values given in Table 3.3). The lower 40% of the water column that remained liquid dropped in temperature by approximately 3°C. As a result, the heat lost from cooling is approximately 3.0 x 10^7 J m^{-2}. This value, while approximate, is nearly an order of magnitude smaller than the calculated heat flux through the surface of the pond. It is clear from these calculations that the latent heat of fusion accounts for the majority, if not all, of the heat lost from the meltwater pond during the freezing process.

Some of the energy derived from latent heat of fusion may have been available to heat the residual fluid underlying the ice in Skua Pond. This would explain the *c.* 6°C increase in temperature recorded at the base of the pond (10 cm above the sediment) while the majority of the water column exhibits cooling (refer to Figure 3.2a). Although latent heat released at the freezing front would slightly increase the temperature of the interfacial fluid, there is potential for this heat to be quickly transported to the underlying fluid through convection. The gravitational instability of the fluid at the freezing front and consequent convection is due to the exclusion of salt from the growing ice. An approximate calculation of the energy required to heat a 10 cm layer at the base of the pond by 6°C (the amount suggested by the temperature record) yields a value of 2.5 x 10^6 J m^{-2}. Therefore only a very small proportion of the latent heat released, needs to be transferred to the basal fluid in order to account for the warming behaviour observed between 500 and 1270 hours. Consequently, the release of latent heat is an important process during meltwater pond freezing with significant implications for geochemical and biological processes.

3.4.3 The Winter Phase

The winter phase takes place from early June to early November, during which time temperatures in the water column in Skua Pond were below freezing and the majority of the pond was assumed frozen (allowing for the possibility of a small volume of basal brine). During this period, temperatures within the water column were driven by changes in air temperature at the pond surface. The close relationship between air temperature and pond surface temperature can be seen by comparing Figure 3.1a and b. Figure 3.1b also shows the response of the underlying layers of ice in the pond as changing air temperatures were communicated downwards. Alternate periods of normal and reverse vertical temperature gradients in the record reflected the interchange between regional warming and cooling events.

A simple one-dimensional diffusion model is proposed here as a tool for exploring the thermal behaviour of the pond in response to the major warming and cooling events observed during the

winter period. The model assumes that molecular diffusion occurs vertically through a homogenous layer of ice, a no-flux boundary condition exists at the base of the pond, the thermal forcing at the pond surface is sinusoidal, and initially the pond ice is assumed to be isothermal in equilibrium with the air temperature. The small layer of liquid brine that may be present beneath the ice at the base of the pond during winter is ignored. Mathematically this model can be stated as

$$\frac{\partial T}{\partial t} = \kappa \frac{\partial^2 T}{\partial x^2} \qquad \textbf{Equation 3. 1}$$

with

$$\kappa \frac{\partial T}{\partial x}(0,t) = 0 \qquad \textbf{Equation 3. 2}$$

$$T(d,t) = T_0 + T_1 \sin \omega t \qquad \textbf{Equation 3. 3}$$

$$T(x,0) = T_0 \qquad \textbf{Equation 3. 4}$$

where T is the temperature within the pond, t is time, x is the vertical coordinate (distance) measured from the base of the pond, κ is the thermal diffusivity of ice, d is the depth of the pond, T_0 is the initial temperature of the ice and air, T_1 is the amplitude of the thermal forcing at the surface and ω is the frequency of the forcing.

An eigenfunction expansion solution to this problem is given by

$$T(x,t) = T_0 + T_1 \sin \omega t + T_1 \sum_{n=0}^{\infty} \frac{4(-1)^n}{(2n+1)\pi \left(1 + \frac{\lambda_n^4}{\omega^2}\right)} \left[\frac{\lambda_n^2}{\omega} \left(e^{-\lambda_n^2 \frac{\kappa t}{d^2}} - \cos \omega t \right) - \sin \omega t \right] \cos\left(\lambda_n \frac{x}{d}\right)$$

Equation 3. 5

where $\lambda_n = \frac{(2n+1)\pi}{2}$. **Equation 3. 6**

Diffusion problems of this sort, where one boundary is sinusoidally forced, are known to exhibit certain characteristics. The thermal response below the surface will have reduced amplitude when compared to the surface forcing itself, and this amplitude decays with distance below the surface, and with increasing forcing frequency. In addition, the maximum/minimum temperature within the ice lags behind that at the surface with the lag reducing as forcing frequency and distance below the surface decrease.

The appropriateness of this model can be tested by comparing the predicted lag between the surface of the pond and the base of the pond, with the lag measured in the field. For this purpose three surface warming events (W1, W2 and W3) and four surface cooling events (C1, C2, C3 and C4) during winter were selected from the temperature record. For each event the forcing frequency, ω, was estimated from the field record, and the phase lag between the temperature maxima/minima at 100 cm and 10 cm above the base of the pond were noted. In each case the air temperature, and ice temperatures throughout the pond, were initially approximately the same. These values, together with the phase lag predicted by the mathematical model using the measured forcing frequencies, are given in Table 3.4.

Table 3.4 Phase lags between thermal maxima and minima at 100 cm and 10 cm above the base of the pond from field measurements and model predictions. H1, H2 and H3 are heating events and C1, C2, C3 and C4 are cooling events. Δt_m is the phase lag predicted by the mathematical model and Δt_f is the phase lag measured in the field.

Event	Approx. Timing (hrs)	ω (hr^{-1})	Δt_m (hrs)	Δt_f (hrs)	$\Delta t_m/\Delta t_f$
W1	3000	0.045	45	42	1.07
W2	3550	0.022	63	63	1.00
W3	4190	0.031	53	66	0.80
				Average	**0.96**
C1	2935	0.062	39	27	1.44
C2	3225	0.018	68	47	1.45
C3	3355	0.070	36	33	1.09
C4	4535	0.070	36	18	2.00
				Average	**1.50**

Average ratios of the predicted phase lag to the measured phase lag for the warming and cooling events were 0.96 and 1.50 respectively. This provides strong support for the underlying assumption that diffusive processes can account for the heat transfer through the ice column during warming events. However, the ratio was significantly different during cooling events where the model consistently predicted phase lags greater than those measured in the field.

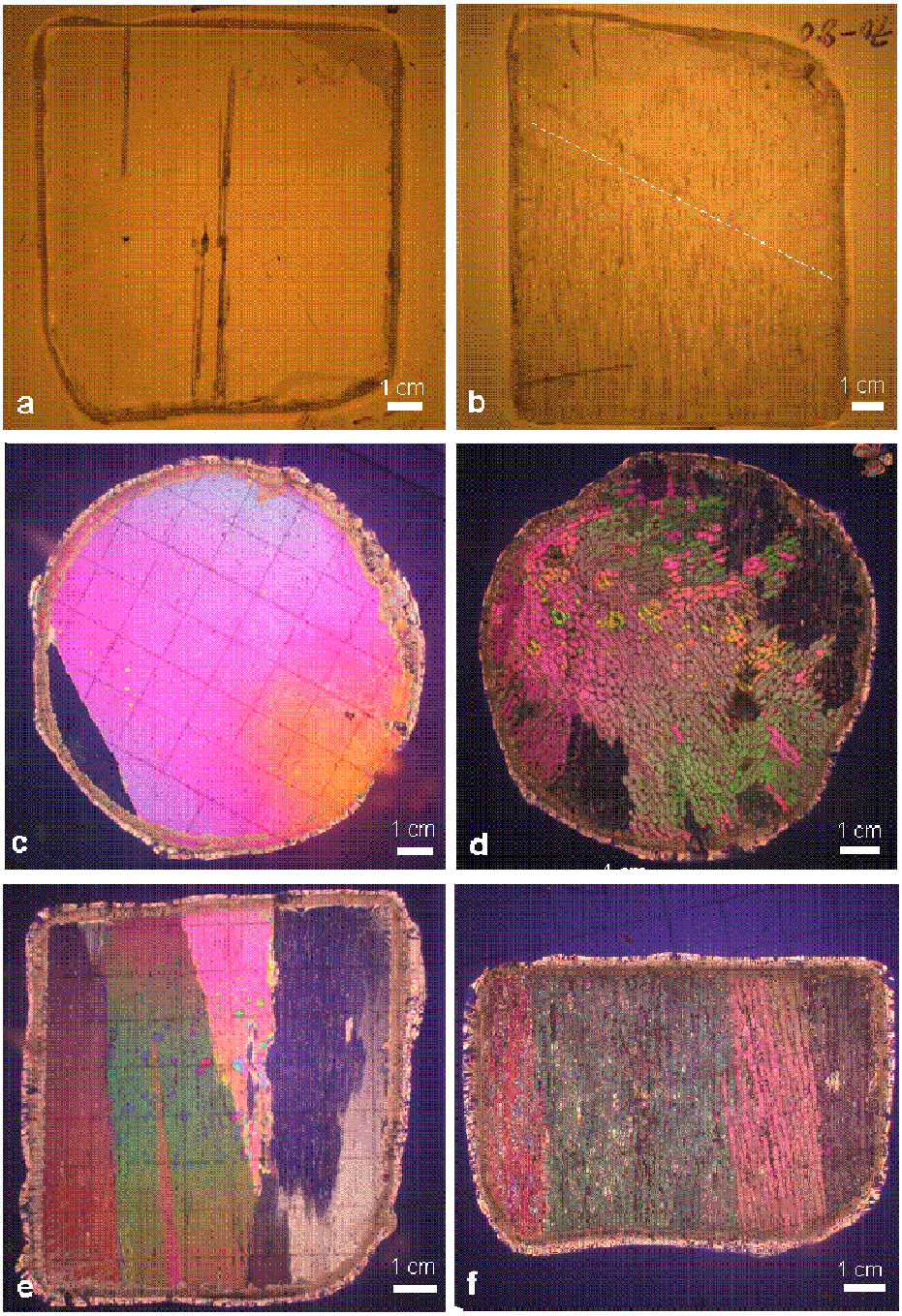

Figure 3.9 Micrographs of Skua Pond ice core; a) longitudinal thick section from 30-40cm depth, b) longitudinal thick section from 70-80cm depth (showing transition between discontinuous and continuous brine phases), c) cross-sectional thin section from 70cm depth, d) cross-sectional thin section from 150cm depth, e) longitudinal thin section from 120-130cm depth, and f) longitudinal thin section from 140-150cm depth. Micrographs a) and b) are shown under transmitted light and the rest under crossed polarised light (copied from Wait *et al.* 2006).

Heat transfer could occur more rapidly during surface cooling events due to the presence of the vertical brine channels within the ice, reported in Wait *et al.* 2006 and shown in Figure 3.9. During cooling events, colder temperatures at the pond surface may lead to weak convection

within the channels, increasing the rate of heat transfer to the pond layers below. During a warming event this mechanism is unavailable due to the stabilising nature of the normal temperature gradient (warmer temperatures overlying relatively cold temperatures). The effectiveness of these brine channels in the heat transfer process will depend on the physical characteristics of the brine channels, such as their diameter, the vertical distances over which they form a coherent conduit, and the viscosity of the brine within them. Consequently, it is not possible to incorporate this mechanism into the mathematical model. However, the likelihood that convection occurs within the brine channels during cooling events is significant in that it leads to the possibility of secondary brine evolution within these channels.

3.4.4 The Thaw Phase

The thaw phase commences in late October / early November as water temperatures approach and begin to exceed 0°C. The temperature profile shown in Figure 3.2b illustrates the complex thawing process that takes place in the pond during melting. While surface cooling is the primary mechanism driving the freezing process, the pond warming and melting process is controlled by a combination of increasing air temperatures and an increase in solar radiation.

In very early summer, temperatures near the surface of the pond rapidly increased in response to rising air temperatures, with the deeper layers in the pond following this overall warming trend through the process of molecular diffusion of heat (as in the winter phase). This resulted in the longest period of normal temperature stratification observed in the record (see Figure 3.2b). Occasional atmospheric cooling events occurred during this period, as well as diurnal temperature fluctuation, preventing a monotonic increase in temperature (see Figure 3.1a).

The temperatures at the base of the frozen pond (i.e. 10 and 20 cm above the base of the pond) respond more rapidly to the warming than those some distance above. This reflects the greater concentration of brine channels in these layers, the possibility of a small volume of basal brine and the depressed freezing points that correspond with these fluids (Wait *et al.* 2006). Therefore little heat is required to transform the saline ice (or ice with significant interstitial brine channels) to a liquid state and latent heat of fusion is not required to raise the temperature above the melting point. Wait *et al.* (2006) reported liquid brine with a temperature of -18°C at the base of Skua Pond in mid-October 2001. In the temperature record presented here, the base of Skua Pond approaches temperatures of -18°C at around 5680 hours (22 October) (Figure 3.2b), therefore it is expected that from this time onwards there may be liquid brine present at the base of the pond. Once liquid is present at the base of the pond it will continue to adsorb heat allowing further temperature increases to occur.

The amount of heating generated by the absorption of solar radiation is expected to decrease with depth as a greater thickness of overlying ice will result in a greater degree of attenuation (Vincent *et al.* 1998). Significant seasonal changes occur in the optical properties of surface ice in some Antarctic lakes when the ice nears 0°C (Fritsen & Priscu 1999). This phenomenon includes ice "whitening", and the formation of candling features, which result in increased attenuation of radiation and an increase in albedo during mid-summer when radiation is at its peak (Fritsen & Priscu 1999). "Meteoric" ice, formed by melting and refreeze of the snowpack on top of a pond also results in opaque ice due to the high density of air bubbles trapped in the ice (Iliescu *et al.* 2002). In addition to the properties of ice that influence solar radiation absorption, the amount of wind blown sediment on or in the pond ice can effectively offset any attenuation (Vincent 1988).

By early November (6000 hours) the rise in air temperature above the surface of the pond had slowed but temperatures measured within the pond continued to increase due to the absorption of solar radiation by the ice, water column and underlying sediments. As thawing of the pond progressed, a pronounced temperature maximum developed 20 cm and 60 cm above the base of the pond (from approximately 6350 hours, Figure 3.2b) suggesting that the absorption of solar radiation down to this level was strong. From this time, temperatures in these layers exceed 0°C and presumably the ice had melted. In contrast, the layer 40 cm above the base of the pond is frozen during the winter months and likely to have fewer brine channels, therefore latent heat of fusion must be supplied before melting can occur. This explains the presence of the ice-plugs observed to remain partway through the water column in ponds that are otherwise fully thawed. Consequently, latent heat plays an important role in determining temperature profiles in meltwater ponds during the thawing phase where the supply of this additional energy is required to bring about the change in phase from winter ice to summer meltwater.

From 6600 hours, the water column 40 cm above the base of the pond also exhibited a temperature maximum, possibly indicating that the middle layers in the pond were mixed. Despite strong absorption of solar radiation in the layers above 60 cm, the thermal gradients in the record suggest that the proximity to the pond surface and the lower air temperatures above the pond results in diffusive heat loss through the pond surface. Consequently, absorption of solar radiation is less effective at warming the ice 80 and 100 cm above the base of the pond.

3.4.5 A Conceptual Model of Meltwater Pond Freeze and Thaw

A key finding of the results presented here is that the process of freezing and thawing in meltwater ponds near Bratina Island differs from the accepted "TDBU" model that has previously

been referred to (e.g. Hawes *et al.* 1999); particularly during the period of pond melt. By correlating physical and chemical observations of meltwater ponds in various states of freeze and thaw with the high resolution record of temperature throughout the year, a new conceptual model of the freeze and thaw process has been developed (Figure 3.10). This model illustrates how chemical stratification is set up during freezing and how stratification may be maintained during summer melt.

Initially, ice forms at the surface of a fully melted pond in response to a drop in air temperature (Figure 3.10a-b). As air temperatures continue to fall the volume of ice increases, growing progressively downwards. During the ice formation process, the majority of salts are excluded and the remaining liquid becomes increasingly saline until dense basal brine is formed (Figure 3.10c-d). An increase in basal water temperature may occur due to the release of latent heat.

Basal brine may or may not freeze (Figure 3.10e), as the freezing point will depend primarily on the salinity of the brine. There is also the possibility that the brine may become super-cooled, remaining as a liquid below its equilibrium freezing point. Schmidt *et al.* 1991 recorded minimum temperatures of -12°C and -13°C at the base of the two ponds at Cape Evans, Ross Island, before the ponds froze solid between mid-winter and late November. Others have recorded temperatures as low as -20˚C and -22˚C in liquid brines of 111 mS cm^{-1} and 148 mS cm^{-1} respectively (Healy *et al.* 2006; Wait *et al.* 2006). The ultimate state of the brine at the base of Skua Pond during the recording period is unknown, but the ability of basal brines in meltwater ponds to freeze solid during winter appears to depend upon a combination of factors including the initial composition of the pond, the effectiveness of salt exclusion, the salinity of the basal brine and the depth of the pond which will determine the degree of insulation provided by the ice column overlying the brine.

Meltwater pond thawing occurs due to the absorption of solar radiation by the ice and the sediments lining the base of the pond. Early melting occurs at the sediment-ice interface in shallow areas of the pond and increases inwards both vertically and horizontally towards the centre of the pond (Figure 3.10f-g), most likely caused by the convection of warmer fluids. This results in a stem of ice connecting an ice plug to the surface ice during the early thaw period (Figure 3.10h). This stem connecting surface ice and the subsurface ice-plug was visible in Eggtimer Pond in December 2005 (Figure 3.11). This stem eventually snaps or melts away, followed by melting of the surface ice to leave just the ice plug near the base of the pond (Figure 3.10i-j). The effect of this thawing phenomenon is significant in that the ice plug separates the winter basal brine from the overlying water column and helps to protect the brine from wind

induced mixing and diffusion. Once the ice plug melts away from the sediments at the edge of the pond it floats to the surface (Figure 3.10k) leaving the dense brine intact at the base of the pond, resulting in summer stratification that may persist until pond refreeze (Figure 3.10l).

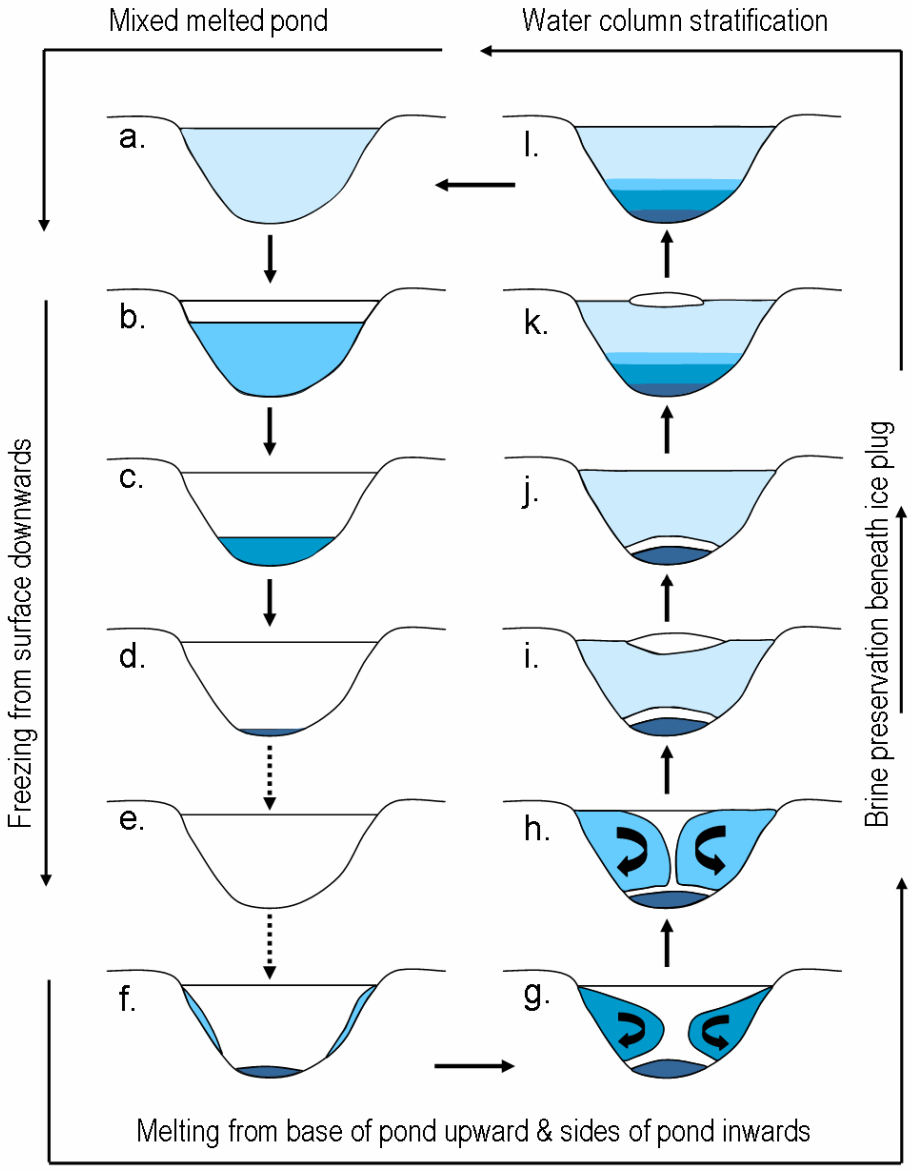

Figure 3.10 Conceptual model of the freeze-thaw process in meltwater ponds and the development of stratification (density of shading reflects the salinity of the water, while white represents ice). Freezing commences in a fully mixed melted pond (a.) from the top down, in response to decreasing air temperatures, excluding salt to form a basal brine (b. – d.) that may or may not freeze (e.). Melting occurs from the base up and sides in (f. – i.) to form an ice plug (j.) which eventually floats to the surface (k.) and melts away leaving a stratified melted pond (l.).

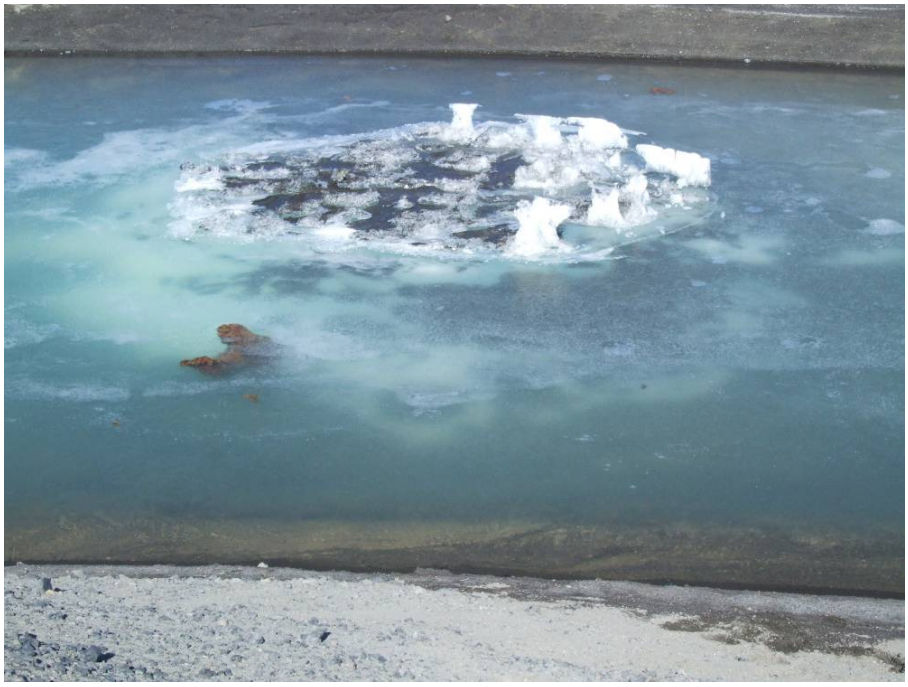

Figure 3.11 Remaining surface ice connected to the subsurface ice-plug in Eggtimer Pond mid-thaw, December 2005.

Meltwater pond thaw is not a one-dimensional process and isotherms are not horizontal within the pond (unlike in some larger ice-covered lakes e.g. Mortimer & MacKereth 1958). This reflects the differential heating of the sediments and the reduced water depth in the littoral zone. Additional high resolution temperature records from littoral areas of the pond would be needed if a more quantitative model of this process is to be produced.

3.4.6 Geochemical Implications of Pond Temperature Regimes

During freezing, pond temperatures control the rate at which ice formation occurs, consequently, the process of salt exclusion from the ice during freezing is also driven by pond temperatures. Increasing salinity during freezing lowers the freezing point of the liquid water, altering the solubility and the saturation point of minerals (e.g. Marion 1997). The depression of freezing point was calculated from the major ion chemistry for a basal brine sample collected from Skua Pond in 2001 (Wait *et al.* 2006). The predicted freezing point was -12.4°C compared to the measured temperature of -18°C, suggesting that there is some other factor influencing the freezing point depression of the brine. A very high total organic carbon concentration of 4640 mg L^{-1} (unpublished data, J. Webster-Brown) was measured in an unfiltered Skua Pond basal brine sample collected in October 2001, most likely concentrated during freezing and unlikely to be significantly utilised by microbes during the winter period. This combined with a strong yellow colouration in the Skua Pond brine (Wait *et al.* 2006) indicates very high concentrations of organic

material. The presence of dissolved organic material in the brine may further depress the freezing point as freezing point depression is a colligative property that depends on the concentration, not the nature, of dissolved ions.

Once most of the water column has frozen, further variation in pond temperature may drive downward convection within the brine channels resulting in secondary brine evolution. This has significant implications for the prediction of basal brine chemistry, which is important for our ability to understand ecosystem functioning during winter, as multiple evolutionary brine processes would need to be accounted for. Pockets of high conductivity brine included in ice midway through the water column (Wait *et al.* 2006) may also be partially explained by this process if convection of brine resulted in further salt exclusion, from the upper layers of ice, which then pooled at the base of the brine channels. Mineral precipitation may also eventuate if concentrations reach saturation with respect to minerals within these evolving brine inclusions.

The presence of ice plugs in meltwater ponds has significant geochemical implications for several reasons. Firstly, it dramatically increases the chance of stratification being preserved during summer, when the ponds are fully melted, compared to relying on density gradients alone to suppress mixing. The presence of summer stratification influences the stability of minerals precipitated during freezing, as well as leading to a greater habitat differentiation for both planktonic and benthic communities (Mueller & Vincent 2006). Secondly, by preserving the anoxic brine conditions at the base of the pond beneath the ice-plug, the time during which anaerobic processes can operate is extended, possibly well into the summer melt period.

Anoxic conditions allow significant H_2S concentrations to be present in some basal brines beneath the pond ice until the release of the ice plug during pond melting. This anoxia and the presence of H_2S combined with high salinity in the basal brines means that the less hospitable winter-type conditions may persist into summer longer than previously thought, effectively shortening the length of time that environmental conditions are favourable for biological production. One of the geochemical implications of this relates to trace metal solubility, as concentrations of trace metals such as Cu, Pb, Zn, and Ni in anoxic Antarctic brines are primarily controlled by the concentration of H_2S (Webster *et al.* 1994; Webster-Brown & Webster 2007). In the presence of even trace concentrations of H_2S, mineral sulfides with these metals will start precipitating, effectively removing metals from the water column. This study has shown that such processes linked to the presence of H_2S may continue for the entire summer melt period, despite high concentrations of dissolved oxygen and an oxidising redox environment, as detectable levels of H_2S (0.02 mg kg^{-1} to 0.33 mg kg^{-1}) were still present in several of the stratified brines at the end

of summer (late January) (Figure 3.6b-c). The presence of coincident H_2S and dissolved oxygen is a thermodynamic anomaly that suggests very slow H_2S oxidation reaction rates. It may reflect the absence or inactivity of sulfur–oxidising bacteria, such as the *Thiobacillus* species that has been found in Lake Fryxell, Antarctica (Sattley & Madigan 2006). It may also indicate a predominance of sulfate-reducing bacteria that continue to produce H_2S at the base of the pond into the summer months. Other reduced sulfur gases, such as dimethylsufide (DMS) and carbon disulfide (CS_2), have also been found dissolved in MIS ponds during the summer period and attributed to biological activity (de Mora *et al.* 1990; de Mora *et al.* 1996). It is unlikely that the measured DO was an artefact as measurements were made insitu with a calibrated meter.

Saturated dissolved oxygen at the base of stratified meltwater ponds soon after ice plug melting (Figure 3.6c) in early summer most likely reflects the commencement of biological processes in the extensive (Vincent 1988; Howard-Williams *et al.* 1989) cyanobacterial mats at the base of the pond once the ice plug has melted away. Cyanobacteria produce dissolved oxygen during photosynthesis; therefore the dissolved oxygen present in the summer brines is probably produced at the base of the pond from increased photosynthesis rather than downward diffusion from the oxygenated water column above. Consequently, it appears that the release of the ice plug also influences the timing of biological processes occurring at the base of the meltwater ponds. A deep peak in dissolved oxygen has also been associated with a photosynthesis maximum in Lake Vanda (Vincent 1981) rather than the result of oxygen diffusion from the surrounding water column. The absence of dissolved oxygen in the basal brines at the end of winter (Wait *et al.* 2006) and immediately after ice plug melting suggests that any increase in dissolved oxygen resulting from freeze concentration (Wharton *et al.* 1987) is lost during the winter period, perhaps by bacterial respiration or sulfide oxidation.

3.5 Conclusions

Seasonal variation in water temperature within meltwater ponds has significant implications for meltwater chemistry and ecosystem functioning. Reverse temperature gradients during freezing and the downward progression of the freezing front drives salt exclusion and in turn influences brine evolution, salt precipitation and the nature of the environmental conditions tolerated by microbiological communities living within these ponds during winter. During both freezing and thawing of meltwater ponds, the release of latent heat of fusion strongly affects thermal gradients within the water column. The most significant feature of the thawing process in early summer that differs from previously accepted TDBU model is the presence of an ice plug which supports the persistence of chemical stratification by creating a barrier to mixing. The ice plug phenomena

also acts as a barrier to chemical processes and lengthens the duration of highly saline anoxic water conditions at the base of the pond during summer. The preservation of anoxic brine beneath ice plugs and the persistence of stratified basal brines during summer have significant implications for microbial communities and the precipitation of certain minerals, potentially influencing the toxicity of the meltwater pond environment.

The relationship between physical and geochemical processes in meltwater ponds is essential to understanding and predicting winter chemical conditions. In particular, the physical and chemical transition of ponds into and out of the winter phase provides clues to the processes that are likely to take place during winter when sampling is limited. Significant findings include:

- The isolation of basal brine beneath an ice plug during melting assists in the preservation of stratification during summer and encourages the persistence of stratification until freezing commences.
- The release of latent heat of fusion increases the likelihood that basal brine remains liquid for much if not all of the year as the base of the pond was warmer that expected during freezing and melting.
- The response of the pond ice to heating and cooling events during winter supports the likelihood that brine channels were present in the ice and therefore that salt exclusion was incomplete.
- Dissolved oxygen is absent from basal brines during winter despite the potential for freeze concentration to take place. Additionally, the ponds remain anoxic until the ice plug is lost at the end of the thaw phase and biological production of DO commences.

CHAPTER 4

MAJOR ION BEHAVIOUR IN THE MELTWATER POND ENVIRONMENT

Figure 4. Free floating meltwater pond ice and salt precipitation (far shore), January 2007.

This Chapter looks at the spatial and temporal geochemical variation that occurs in Bratina Island meltwater ponds during the transition from the thaw phase to the summer phase when ponds have just become ice-free, the summer phase when the ponds are at maximum melt and have been ice-free for some time, and finally during the freezing phase as an ice cover forms on the surface of the ponds and progressive freezing develops. Water sampling includes collection from different water column heights in each pond in order to characterise the stratification that may be present, encapsulating the chemistry of the pond as a complex system rather than a homogeneous water body.

4.1 Context of this Research

4.1.1 Major Ion Composition of Antarctic Meltwater Ponds

The earliest studies of meltwater pond composition focused on the highly saline Don Juan Pond in the Wright Valley, McMurdo Oasis (Morrow *et al.* 1962; Webster & Goguel 1988, Webster 1993). Don Juan Pond is a shallow water body (~10cm deep) that covers an area 100m by 300m that generally remains in a liquid state even at temperatures as low as -51°C. Concentrations of major ions from these studies are included in Table 4.1. This Ca-Cl dominated pond is thought to have developed as a result of groundwater inflow from which the less soluble salts mirabilite ($Na_2SO_4.10H_2O$) and halite (NaCl) had already precipitated (Webster *et al.* 1993) and consequently the concentrations of other ions are low relative to Ca and Cl (see Table 4.1).

This was followed by a study of the water chemistry of 54 ponds in the Labyrinth, Victoria Land, where a single water sample was taken from each pond (Torii *et al.* 1989). Results indicate that all but 5 ponds were Na-Cl dominated, with the others being dominated by Na-SO_4. The compositional range of these ponds is shown in Table 4.1. Saline meltwater ponds in the Victoria Valley and Bull Pass regions in Victoria Land were also sampled by Webster *et al.* 1994. The Ca-Cl brine found in the Wright Valley (Webster 1993) was not present in these ponds, instead Na was the dominant cation and Cl or HCO_3 the dominant anion (Table 4.1).

The first detailed investigation into the limnological properties of meltwater ponds looked at the basal water chemistry of two coastal ponds on Ross Island, every two weeks during winter freezing and spring melting (Schmidt *et al.* 1991). This study recorded the increasing conductivity and decreasing temperatures beneath the ice during freezing. Major ion concentrations increased progressively during freezing (maximum concentrations given in Table 4.1) but SO_4 peaked in May/June then fell reportedly as a result of mirabilite precipitation (Schmidt *et al.* 1991).

The first comprehensive survey of the chemical composition of surface water in meltwater ponds on the MIS was undertaken by de Mora *et al.* (1994). Meltwater ponds were found to differ in morphology, biology and chemistry depending on the type of ice shelf terrain they were found on, with two distinct pond types having been identified - pinnacle ice ponds and ice-cored moraine ponds (Howard-Williams *et al.* 1990; de Mora *et al.* 1994). Pinnacle ice areas had sparse sediment cover and large amounts of exposed ice, little or no cyanobacterial mats and ponds that tended to be small and shallow. This environment showed a high degree of short term environmental change in the form of melting, deterioration and collapse. Ice-cored moraine areas were characterised by a 10-20 cm sediment layer covering a hummocky ice shelf surface.

Table 4.1 Concentrations (in mg kg^{-1}) of major ions in Antarctic meltwater ponds by region (MIS = McMurdo Ice Shelf) from previous studies.

Field Area	Na	K	Ca	Mg	Cl	SO_4	HCO_3	NO_3	Reference
Don Juan Pond, Wright Valley	11500 - 15000	127 - 160	106800 - 114000	1200 - 1930	190000 – 212000	11 – 79.9	45.8		Morrow *et al.* 1962; Webster & Goguel 1988; Webster 1993
Labyrinth, Victoria Land	4.8 - 24200	0.54 - 465	1.1-1240	1.1-10300	4.9 - 52400	3.0 - 12100			Torii *et al.* 1989
Labyrinth (surface water)	74 - 7530	1 - 76	25 - 116	21 - 3280	67 - 15200	181 - 2840	1 - 261	55 - 9730	Healy *et al.* 2006
Labyrinth (basal water)	608 - 11400	1 - 111	63 - 825	148 - 7240	520 - 26800	1090 - 11400	10 - 984	486 - 16800	Healy *et al.* 2006
Cape Evans, Ross Island	52000	4100		9000	110000	17000			Schmidt *et al.* 1991
Darwin Glacier region	1.2 - 780	0.2 - 160	0.8 – 300	0.2 - 340	1.5 - 2000	1.2 - 533	2.0 - 60	0.05 - 1300	Vincent & Howard-Williams 1994; Timperley 1997
Bull Pass	56.6 - 675	5.27 – 26.1	9.76 - 501	12.2 - 430	108 - 2560	11.0 - 312	27.0 - 152		Webster *et al.* 1994
Bratina Island, MIS (surface water)	5.06 - 21404	0.391 - 454	0 - 232	0.486 - 478	5.32 - 7126	0.961 - 30836	85.3 - 207		de Mora *et al.* 1994; Vincent & Howard-Williams 1994; Wait *et al.* 2006
Bratina Island, MIS (basal water)	226 - 18700	8.1 - 267	13.5 - 892	9.5 - 997	134 - 11500	241 - 33900	63 - 219		Wait *et al.* 2006
Victoria Valley (surface water)	40.0 - 1960	1.51 – 51	12.6 - 1230	0.49 - 1570	40.1 - 6210	37.8 - 1600	38.2 - 147	251 - 1050	Webster *et al.* 1994; Healy *et al.* 2006
Victoria Valley (basal water)	1960 - 6560	61 - 202	573 - 3680	760 - 4120	5100 - 25100	1540 - 2320	8 - 106	723 - 4330	Healy *et al.* 2006

Extensive cyanobacterial mat communities were present in the numerous meltwater ponds in the depressions on the ice shelf surface. This environment was more stable than that of the pinnacle ice terrain (de Mora *et al.* 1994). The surface water of meltwater ponds on the MIS was found to be dominated by the Na cation followed by Mg, Ca and K, either Cl or SO_4 was the dominant anion (de Mora *et al.* 1994). It was noted that concentrations of Na, K and Mg followed the distribution pattern of Cl in dilute samples suggesting that they were predominantly of sea water origin, however Na and K were relatively enriched compared to seawater in samples of higher ionic strength (de Mora *et al.* 1994). Proportionally greater concentrations of SO_4 and Ca than in seawater were attributed to the contribution of marine derived gypsum (de Mora *et al.* 1994). The major ion concentrations measured in the de Mora *et al.* (1994) study are presented in Table 4.1.

Another early study of meltwater pond composition compared the major ion concentrations in Bratina Island meltwater ponds on the MIS to those in the Darwin Glacier region 300km further south at 80˚S (Vincent & Howard-Williams 1994). Once again Na and Cl or SO_4 were identified as the dominant ions in MIS ponds. In the Darwin Glacier region it was found that Na was generally the dominant cation, however Ca was an important and sometimes dominant cation in these ponds. As in the MIS ponds, Cl tended to be the dominant anion but SO_4 was near equal in concentration or dominant in some cases (Timperley 1997; Vincent & Howard-Williams 1994).

The early sampling of meltwater pond water for compositional analysis, as described above, took samples from the surface water layer only. The studies by Wait *et al.* 2006 and Healy *et al.* 2006 were the first comprehensive studies of meltwater composition at different depths in the water column taking into account the chemical stratification of ponds that had been mentioned in Webster *et al.* (1994), Hawes *et al.* (1997) and Downes *et al.* (2000), as well as the temporal changes in chemistry that arise from the freeze – thaw process (e.g. Schmidt *et al.* 1991).

When fully thawed in summer, Bratina Island ponds showed increasing concentrations of ions with depth, with stratification being retained due to the strong density gradient resulting from the presence of highly saline basal brines (Wait *et al.* 2006). Summer brine layers were either SO_4 or Cl dominated while Na was the dominant cation in all samples collected from the Bratina Island area. Meltwater ponds in the Victoria Valley and Labyrinth in Victoria Land also showed increasing major ion concentrations with depth resulting in the formation of basal brines similar to those seen in Bratina Island ponds (Healy *et al.* 2006). These basal brines were also Na – Cl dominated, often showing depletion of SO_4, but were enriched in NO_3 compared to Bratina Island ponds (Healy *et al.* 2006).

Sources of Solutes in Meltwater Ponds

Variation in the chemistry of meltwater ponds is the result of numerous processes as described in Chapter 1.2.1. In summary, there are several possible sources of solutes in coastal meltwater ponds as follows (de Mora *et al.* 1994):

- Atmospherically-derived material;
- Sea water ions via precipitation, direct input and sea ice melting.
- Chemical weathering of geological material, including the dissolution of recent salt deposits.

In and around meltwater ponds on Ross Island (Schmidt *et al.* 1991) and on the MIS (Wait *et al.* 2006) mirabilite is the dominant salt mineral observed in the soil. Compared to the ratio of major ions to Cl in seawater, the Bratina Island meltwaters are proportionally enriched, particularly in the case of SO_4, although not necessarily found in higher concentrations than sea water. This appears to be the product of melting sea ice that has undergone varying degrees of desalination (de Mora *et al.* 1994). The relative enrichment of SO_4:Cl in meltwater compared to seawater is attributed to the dissolution of mirabilite deposits in the local area. Despite the proximity of Mt Erebus and other volcanic cones in the McMurdo Sound area, volcanogenic ions, especially Cl and SO_4, have not significantly contributed to the salt phases on the MIS (Keys & Williams 1981).

In MIS ponds, the Mg:Ca ratio is varied while the Mg:Na ratio is low suggesting that the salt in the ponds is of marine origin with different ponds having undergone varying degrees of evaporation and re-dissolution, and that weathering is of little importance as a source of ions in these ponds (Vincent & Howard-Williams 1994). In the Darwin Glacier region, ratios of Mg:Ca were similar to those on the MIS (indicating evaporation and dissolution) but the ratio of Mg:Na was much higher indicating that weathering within the pond catchment has contributed to the salts present in the pond (Vincent & Howard-Williams 1994). Meltwater ponds in the Darwin Glacier region were also investigated by Timperley 1997 and the major ion composition (see Table 4.1) of the ponds again indicates significant interaction with soil salts and weathering products, and preferential transport of more soluble ions to the meltwater ponds.

Chemical weathering of minerals such as calcite, mirabilite, gypsum and halite provide an inland source of solutes (Green *et al.* 1988; de Mora *et al.* 1994). With increasing distance from the sea, an increasing proportion of NO_3 and SO_4 salts compared to Cl salts have been observed in soils (Keys & Williams 1981). This is indicative of either the precipitation of sea salts that deplete Cl as the distance from the sea increases (Keys & Williams 1981), and/or an inland source of NO_3 and

SO_4 that contributes proportionally more as the distance from the sea increases (Timperley 1997). For example NO_3 can be derived from darapskite and nitratine, while SO_4 can be derived from thenardite and gypsum present in the Labyrinth and Victoria Valley soils (Healy *et al.* 2006). Atmospheric or stratospheric aerosol salts such as HNO_3 and $(NH_4)_2SO_4$, rather that marine aerosols, are thought to be the original source of NO_3 and SO_4 in inland areas (Campbell & Claridge 1977, Vincent & Howard-Williams 1994). Consequently, meltwater ponds are relatively enriched in SO_4 and NO_3 as distance from the sea increases.

In the Wright Valley, Victoria Land (the location of Don Juan Pond), salts are derived from chemical weathering of bedrock and sediments and/or atmospheric precipitation that is transported via summer meltwater of glacial or snow origin (Wilson 1964; Wilson 1979; Webster & Goguel 1988). Preferential transport of the least deliquescent salts (a geochemical separation system) results in the high concentrations of Ca compared to Na and depleted SO_4 in Don Juan Pond (Wilson 1964; Wilson 1979; Webster & Goguel 1988).

Given the reasonably close proximity of ponds to each other within each meltwater pond region (e.g. Bratina Island ponds, Figure 2.1, Chapter 2), it would be expected that atmospheric deposition of salts and the rate of weathering processes within a catchment would result in ponds of similar composition. However, the wide variety of pond chemical compositions within each region or localised area (see Table 4.1) indicates that this is not the case. Reasons for this include varying rates of ion mobility through the soil in a catchment; for example Cl and NO_3 ions are more mobile whereas CO_3 and SO_4 are largely retained in the soil (Timperley 1997), and internal pond processes such as freeze concentration and salt precipitation (e.g. Healy *et al.* 2006; Wait *et al.* 2006).

4.1.2 Geochemical Processes during Downward Freezing

The fundamental process that occurs in a meltwater pond during winter is the change from a liquid state to a solid state by the process of freezing, as extensively described in Chapter 3. There are several key features of the freezing process in meltwater ponds that affect pond geochemistry including:

- Cooling of the water body from the surface downwards (as described in Chapter 3, see Figure 3.2a);
- Partitioning of ions between the solid and liquid phase (discussed below);
- Brine formation by the process of salt exclusion (as described in Chapter 3); and
- Saturation of ions leading to mineral precipitation.

Water and ice chemistry evolves during freezing depending on the partitioning of solutes at the ice-water interface (i.e. the freezing front). Theoretically, there would be no incorporation of solutes into the ice phase during solution freezing in a closed system with concentrations of conservative ions and dissolved gases increasing linearly in proportion to the concentration factor (the ratio of initial to final volume) until mineral precipitation and gas bubble nucleation resulted in solution evolution (Killawee *et al.* 1998). In reality, impurities are found to be ubiquitous in natural ice (Illiescu *et al.* 2002). The concentration of ions at the interface between the freezing front and the residual fluid increases with time due to increased solute rejection (Grange *et al.* 1976) increasing the chance of impurities being incorporated in the newly formed ice.

When freezing brackish or saline solutions, such as the water found in meltwater ponds, the effectiveness of solute exclusion from the ice is dependant upon the presence of convection, solution agitation, and the freezing rate (Cragin 1995). Ice-cover precludes wind and wave induced turbulent mixing of a water body over winter when strong winds are most frequent in Antarctica (Ferris *et al.* 1991) consequently, solution agitation is less of a consideration in meltwater pond environments. However, the progressive increase in ice-volume and brine exclusion can produce vertical convective mixing in the under-ice water column due to the higher density of the excluded salts compared to the density of the unfrozen water (Ferrick *et al.* 2002) to a depth at least as great as wind-induced turbulence (Ferris *et al.* 1991). In the absence of convection, progressive freezing results in a greater incorporation of solutes in the ice as solutes concentrating at the ice-water interface can only be removed by diffusion.

Table 4.2 Concentrations of major ions (in mg kg^{-1}) at the surface and base of Bratina Island (BI) ice cores and in BI (Wait et al. 2006)and Labyrinth (Healy et al. 2006) basal brine in meltwater ponds sampled in late winter. nm indicates not measured.

Field Area	Na	K	Ca	Mg	Cl	SO_4	HCO_3	NO_3
BI surface ice	1.26 - 13900	<1 – 207	<1 – 91.2	<1 - 484	1.48 - 6730	0.3 - 20800	nm	nm
BI basal ice	4100 - 14300	128 - 520	42.5 - 111	484 - 1030	6440 - 16800	1370 - 12000	nm	nm
BI basal brine	54100 - 72500	1680 – 5550	3.19 - 7520	1850 - 7890	110000 - 135000	1310 - 3640	488 - 9570	nm
Labyrinth basal brine	39800 - 60600	1370 - 2140	2370 - 4000	19900 - 23800	85200 - 98800	3160 - 5480	1650 - 3190	65900 – 83300*

*The origin of high NO_3 concentrations are discussed in Section 4.1.1.

The exclusion of dissolved salts from ice into the residual water body is an important process that accompanies ice formation, and the closed nature of meltwater ponds can result in the formation of highly saline basal brine and the precipitation of minerals (e.g. Healy *et al.* 2006; Wait *et al.*

2006). Ice core samples and residual fluid collected from Bratina Island and Labyrinth (Victoria Land) ponds prior to summer melt, showed an increase in major ion concentration in the ice with depth (see Table 4.2), consistent with a progressive freeze concentration of the solution (Healy *et al.* 2006; Wait *et al.* 2006). In both localities the residual brines, where present, were Na-Cl dominated (Healy *et al.* 2006; Wait *et al.* 2006).

Once solutes are sufficiently saturated, mineral phases can begin to precipitate. Mineral precipitated in the soils in and around Bratina Island meltwater ponds include mirabilite ($Na_2SO_4.10\ H_2O$), thenardite (Na_2SO_4 - dehydrated mirabilite), halite (NaCl) and dolomite (Wait *et al.* 2006). Gypsum was identified in samples from the base of MDV's meltwater ponds (Healy *et al.* 2006). Salt precipitation can also occur as meltwater ponds evaporate and concentrate into a saline brine. For example, samples collected from the centre of a dry ephemeral pond in the MDV's identified the minerals hexahydrite ($MgSO_4.6H_2O$), blödite ($Na_2Mg(SO_4)_2.H_2O$), iöweite ($Na_{12}(Mg_7(SO_4)_{13}.15H_2O$) and gypsum, with thenardite, darapskite ($Na_3(NO_3)(SO_4).H_2O$), nitratine ($NaNO_3$) and occasionally gypsum and halite around the edges (Healy *et al.* 2006).

4.1.3 Contribution of this research

In the previous chapter, four distinct temperature phases that occur annually within meltwater ponds were identified (a Freezing Phase, a Winter Phase, a Thaw Phase and a Summer Phase). These four phases reflect the physical processes operating in the ponds with significant implications for the geochemical processes occurring at that time.

This research looks at the spatial and temporal geochemical variation that occurs in Bratina Island meltwater ponds at three different time periods in order to further understand the geochemical processes occurring during these phases. Firstly, the transition from the thaw phase to the summer phase (December 2005) when ponds have just become ice-free. Secondly, the summer phase when the ponds are at maximum melt and have been ice-free for some time, and finally the freezing phase as an ice cover forms on the surface of the ponds and progressive freezing develops. These three phases provide a context for understanding and predicting winter conditions by highlighting conditions going into and coming out of the winter phase.

These first two time periods are viewed as a snapshot of what occurs during that phase with a single "static" sampling event for each. Repeated sampling during the "dynamic" freezing phase improves our understanding of the temporal geochemical variation that occurs in meltwater ponds at a time when physical and geochemical change is significant. Additionally, water sampling includes collection from different water column heights in each pond in order to characterise the

stratification that may be present, encapsulating the chemistry of the pond as a complex system rather than a homogeneous water body.

For the purposes of this chapter meltwater ponds are viewed as closed systems with respect to mass. Additionally, this research focuses on the ice-cored moraine type meltwater ponds (hereinafter referred to simply as meltwater ponds); pinnacle ice ponds are no longer included in this discussion.

4.2 Data Collection

Water samples were collected by the author at Bratina Island in December 2005 when the study ponds first melted completely, and in January 2007 when the ponds had been fully melted for some time. Water samples were also collected by Dr Ian Hawes and Karl Safi (NIWA) from the same ponds repeatedly between February and April 2008 when the ponds were refreezing. Samples from 2005 and 2007 were stored and transported back to NZ where they were analysed for major ions (Na, K, Mg, Ca, Cl, SO_4, HCO_3) using HPIC, AAS and titration. A description of these analytical techniques is given in Chapter 2.3.1 and 2.3.3. Samples collected in 2008 were mainly analysed by Drs Jenny Webster-Brown and Kevin Brown using these same methods, and the data made available to this study.

In order to determine the types of minerals that were present near meltwater ponds, a selection of sediment samples were collected from in and around Bratina Island meltwater ponds in December 2005 and January 2007 and analysed using SEM (described in Chapter 2.3.6).

4.3 Results

4.3.1 Geochemistry of Ponds in the late Thaw Phase

Sampling took place in December 2005 to coincide with the end of the thaw phase and the start of the summer phase as the ponds had just completed melting. The physical and geochemical parameters that were measured in the field in ponds near Bratina Island are given in Table 4.3 and Table 4.4. Although not strictly a physical parameter, conductivity is included here to give an indication of total ion concentration in the water sample.

Electrical conductivity in the ponds ranged from 2.1 mS cm^{-1} measured at the surface of Huey Pond to 74 mS cm^{-1} measured at the base of P70 Pond. The pH of the meltwater was alkaline ranging from 7.95 to 9.94 and DO ranged from 1 to >20 mg L^{-1} (exceeding the instrument limit). Water temperatures were variable ranging from 3.5˚C to 9.4˚C. Conductivity showed a significant increase with depth in all ponds, whereas pH and temperature tended to slightly decrease. Dissolved oxygen concentrations were very low at the base of Upper and Huey Ponds compared

to the well oxygenated surface waters, when sampling took place immediately following ice plug release. Conversely, P70 Pond and P70E Pond were sampled soon after (i.e. within 24 hours) but not immediately following the ice plug release showed increasing DO at the base of the pond. This was particularly apparent in P70E Pond where DO reached the instrument limit of 20 mg L^{-1}.

Table 4.3 Physical parameters measured in Bratina Island meltwater ponds in December 2005. Insitu measurements were made at the temperate presented.

Pond	Depth	Height above Sediment	Temp	EC	pH	DO
2005	cm	cm	°C	mS cm^{-1}	pH units	mg L^{-1}
Upper	20	42	4.9	7.5	9.88	13.9
	35	27	5.1	13.6	9.94	7.6
	45	17	5.1	16.5	9.90	4.7
	55	7	4.7	26.6	9.71	1.3
	61	1	3.8	39.3	9.65	1
Huey	20	30	9.4	4.17	9.58	12.9
	40	10	9.4	16.5	9.39	6.2
	45	5	8	32.3	9.44	2.3
	49	1	6.9	41.8	9.37	1.27
P70	40	46	7.5	4.78	9.32	12.3*
	85	11	7.5	5.02	9.38	12.3*
	90	6	7.1	5.5	9.49	13.6*
	95	1	6.5	74	7.95	14.5*
P70E	20	46	4	6.17	8.60	12.6
	40	26	3.5	7	8.81	15.8
	50	16	6.5	22.5	8.80	>20
	60	6	5	34.6	8.12	16.8
	66	1	4	55	8.20	20

* DO measurements were unable to be taken *in situ* for this sample; this result is measured in a water sample extracted using a hand vacuum and is likely to have undergone some degassing.

In all four study ponds, Na was the strongly dominant cation, followed by Mg and then K or Ca, and Cl was the dominant anion followed by SO_4 and then HCO_3. Concentrations of Na ranged from 680 mg kg^{-1} measured at the surface of Huey Pond in 2005 to 22700 mg kg^{-1} at the base of P70 Pond. Concentrations of Mg ranged from 50.1 mg kg^{-1} to 3040 mg kg^{-1}, K from 25 mg kg^{-1} to 735 mg kg^{-1} and Ca from 17 mg kg^{-1} to 2110 mg kg^{-1}. Concentrations of Cl ranged from 1110 mg kg^{-1} in Huey Pond to 36600 mg kg^{-1} at the base of P70 Pond. Concentrations of SO_4 ranged from

146 mg kg^{-1} to 6880 mg kg^{-1} and HCO_3 ranged from 61.3 mg kg^{-1} to 2330 mg kg^{-1}. Stratification of major ion concentrations with depth is shown in Figure 4.3.

Table 4.4 Major Ion Chemistry of Bratina Island Meltwater Ponds in December 2005

Pond	Height above Sediment	Na	K	Mg	Ca	Cl	SO_4	HCO_3
2005	cm	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
Upper	42	1720	41.0	50.1	27.0	1730	1060	308
	27	3320	71.0	84.8	24.0	3030	2480	576
	17	4050	88.0	110	23.0	3770	3310	686
	7	7810	195	221	18.0	9160	4660	1470
	1	11700	290	333	17.0	13200	6574	2330
Huey	30	680	25.0	89.3	38.0	1110	192	107
	10	3480	130	420	53.0	5580	722	289
	5	7310	293	1020	56.0	13700	1960	689
	1	10200	393	1420	62.0	18300	2490	796
P70	46	856	34.0	112	34.0	1420	195*	136
	11	877	35.0	113	36.0	1510	203*	143
	6	985	41.0	121	40.0	1640	217*	158
	1	22700	735	2810	353	36600	6880	2320
P70E	46	844	31.0	187	149	1980	146	61.3
	26	837	32.0	185	148	1980	150	62.2
	16	3560	123	812	609	8200	558	80.4
	6	7680	245	1810	1400	17600	1000	225
	1	12000	385	3040	2110	28600	1790	270

*Although SO_4 appears more dominant than HCO_3 when compared on a weight basis, the reverse is true on a molar basis.

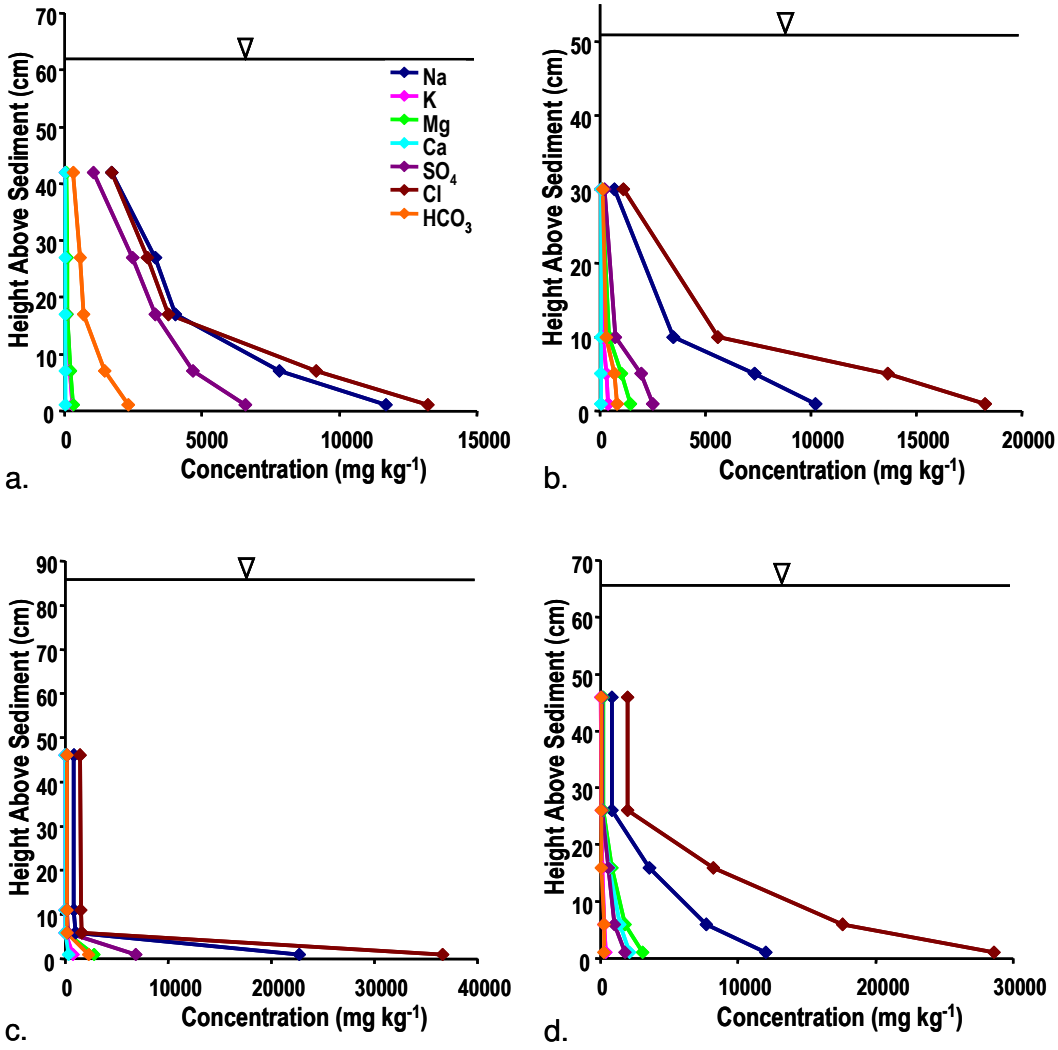

Figure 4.1 Major ion concentrations with depth in four, fully melted, stratified Bratina Island meltwater ponds; a. Upper Pond; b. Huey Pond; c. P70 Pond; d. P70E Pond as sampled in December 2005. The horizontal line and inverted triangle symbol indicate water level at time of sampling with the upper data point representing a sample of the mixed surface layer.

The maximum depth of each pond is given for 2005 and 2007 in Table 4.5.

Table 4.5 Maximum depths (m) recorded in meltwater water ponds near Bratina Island in December 2005 and January 2007 (nm – not measured).

Pond	Depth (2005) (m)	Depth (2007) (m)
Huey	0.5	0.53
P70	0.96	1.1
P70E	0.66	0.81
Upper	0.62	0.67
VXE6	nm	0.92
Eggtimer	nm	1.55
Orange	nm	1.28

4.3.2 Geochemistry of Ponds in the Summer Phase

Sampling took place in January 2007 during the summer phase when the Bratina Island meltwater ponds had been fully melted for some time. The physical and geochemical parameters that were measured are given in Table 4.6 and Table 4.7.

Table 4.6 Physical parameters measured in Bratina Island meltwater ponds in late January 2007. nm indicates that DO was 'not measured' in some ponds due to technical problems with the DO meter in the field.

Pond	Depth	Height above Sediment	Temp	EC	pH	DO	Eh
2007	cm	cm	°C	mS cm^{-1}	pH units	mg L^{-1}	mV
Upper	20	48	4.4	4.51	10.1	12.6	319
	50	18	8.3	16.3	9.72	12.9	347
	65	3	11.5	36.1	9.50	12.7	361
Huey	25	28	7.7	3.68	10.1	12.2	234
P70	10	93	6.5	3.86	9.62	nm	247
	60	53	6.2	3.86	9.67	nm	236
	110	3	5.9	3.93	9.69	nm	240
P70E	20	61	8.7	5.66	8.65	11.4	281
	78	3	7.2	35.1	9.01	12.6	255
Orange	50	78	4.2	2.1	9.82	nm	232
	120	8	4.5	6.28	9.68	nm	245
	125	3	4.9	32.2	9.21	nm	244
VXE6	30	62	4.8	5.74	9.02	10.4	295
	85	7	5.2	19.8	9.54		-
	89	3	5.8	35.2	10.2	12.0	274
Eggtimer	50	104	5.4	2.5	9.00	11.6	303
	130	24	7.7	19.6	8.99	11.1	330
	140	14	8.8	40.4	8.41	nm	338
	151	3	7.3	64.1	8.03	14.1	345

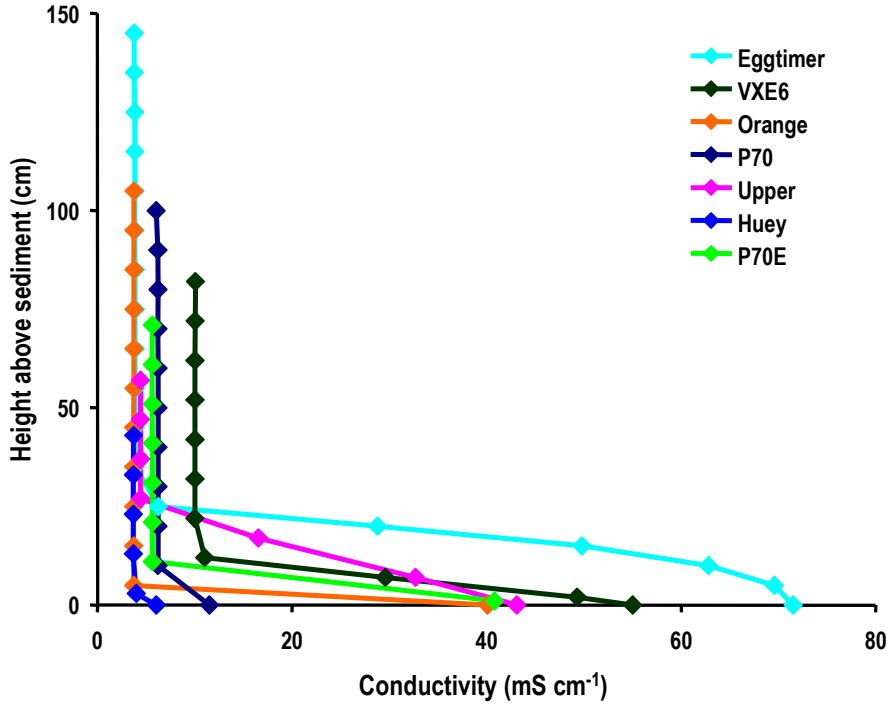

Figure 4.2 Conductivity stratification in Bratina Island meltwater ponds sampled in January 2007.

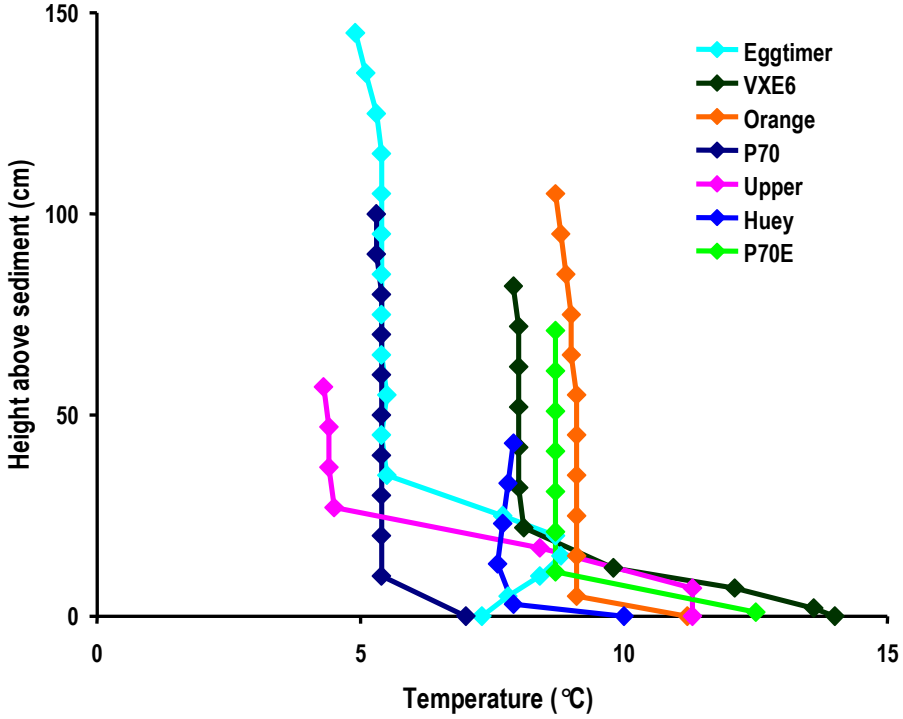

Figure 4.3 Temperature stratification in Bratina Island meltwater ponds sampled in January 2007.

Table 4.7 Major Ion Chemistry of Bratina Island Meltwater Ponds in January 2007.

Pond	Height above Sediment	Na	K	Mg	Ca	Cl	SO_4	HCO_3
2007	cm	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
Upper	48	1210	33.5	34.7	17.7	1200	861	286
	18	5890	146	168	20.0	6480	3210	1200
	3	14200	321	385	0.962	14000	10000	2810
Huey	28	921	41.2	100	39.0	1550	199	85
P70	93	1020	41.1	103	40.8	1670	250	121
	53	1060	40.9	108	43.2	1740	252	119
	3	991	41.9	116	43.2	1710	264	122
P70E	61	1080	41.8	210	201	2270	155	94
	3	5790	230	1360	1720	13900	1240	66
Orange	78	656	27.0	40	14.6	847	151	295
	8	2100	79.5	118	8.4	2530	439	2450
	3	10900	451	536	19.3	12800	2440	5780
VXE6	62	1330	50.5	195	150	1980	640	100
	7	2530	145	643	566	4520	1510	121
	3	7680	286	1080	907	12400	3520	94
Eggtimer	104	713	25.2	75.1	30.1	1230	175	189
	24	5710	183	528	80.8	9780	1320*	1170
	14	14200	394	911	129	21900	2990	3020
	3	23300	650	1640	189	36900	7280*	5610

*Although SO_4 appears more dominant than HCO_3 when compared on a weight basis, the reverse is true on a molar basis.

Electrical conductivity in the ponds ranged from 4.17 mS cm^{-1} measured at the surface of Orange Pond to 64.1 mS cm^{-1} measured at the base of Eggtimer Pond. The pH of the meltwater was alkaline ranging from 8.03 to 10.2 and DO ranged from 10.4 to 14.1 mg L^{-1}. Water temperatures were variable ranging from 4.2˚C to 11.9˚C. Stratification was apparent as physical parameters changed with depth. Conductivity showed a significant increase with depth in the stratified ponds, while it remained constant in mixed ponds (e.g. P70 Pond).

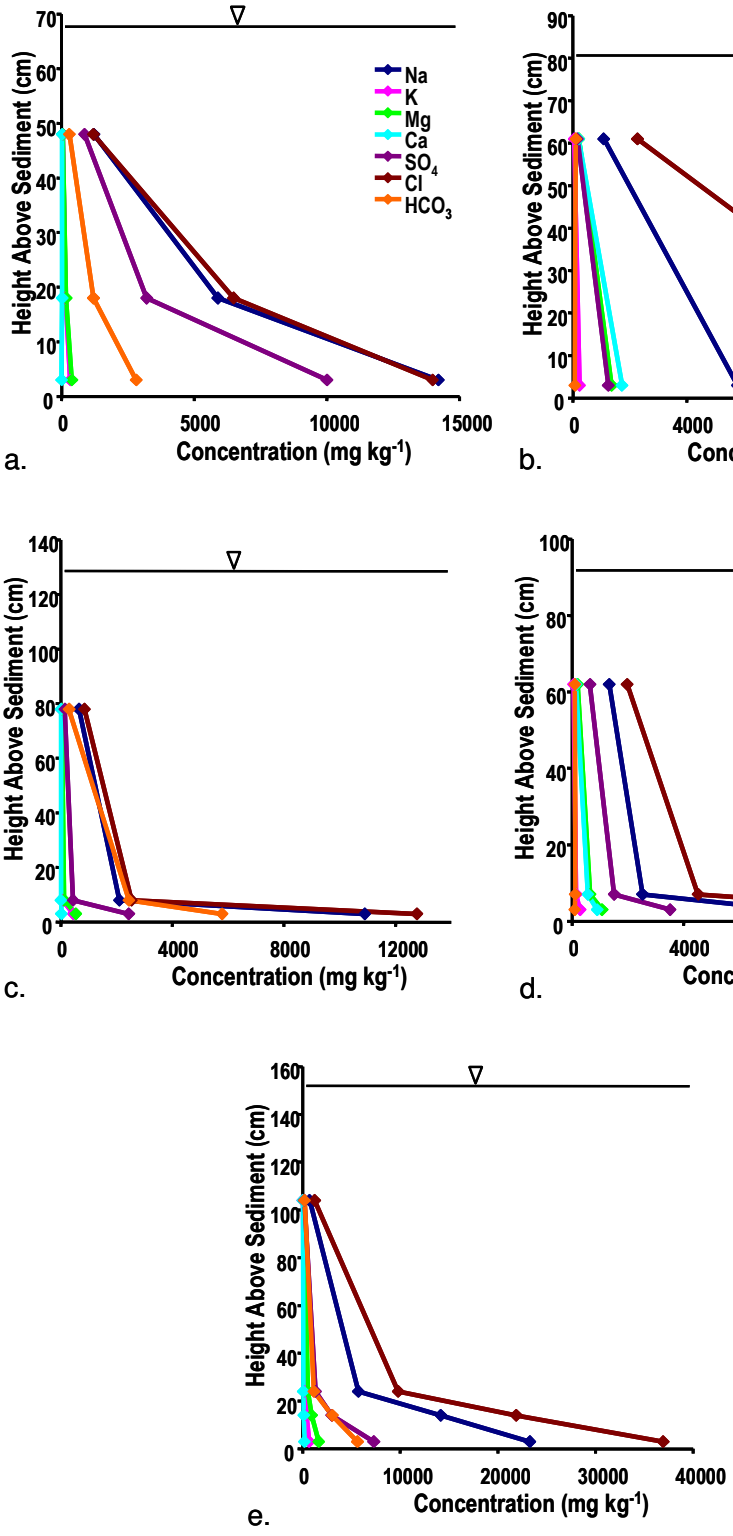

Figure 4.4 Major ion concentrations with depth in five, fully melted, stratified Bratina Island meltwater ponds sampled in January 2007; a. Upper Pond; b. P70E Pond; c. Orange Pond; d. VXE6 Pond; e. Eggtimer Pond. The horizontal line and inverted triangle symbol indicate water level at time of sampling with the upper data point representing a sample of the mixed surface layer.

P70E and VXE6 Ponds showed an increase in pH with depth and Upper and Eggtimer Ponds showed a decrease in pH with depth, while P70 and Orange Ponds showed no change. Redox (Eh) generally showed the reverse trend to pH with P70E and VXE6 Ponds showing a decreasing in Eh with depth and Upper and Eggtimer Ponds showing an increase, while P70 and Orange Ponds again showed no change. Upper, VXE6 and Eggtimer Ponds had higher temperatures at the base of the pond compared to the surface water while P70 and P70E Ponds showed a decrease in temperature at the base of the pond.

In addition to measurements taken at the time of water sampling (i.e. Table 4.3), higher resolution profiles of conductivity and temperature were taken *in situ* as shown in Figure 4.1 and Figure 4.2 (data is presented in Appendix 2). These profiles show the distinct stratification present in the ponds. As in earlier samples, Na was the strongly dominant cation followed by Mg and then K or Ca. Concentrations of Na ranged from 656 mg kg^{-1} measured at the surface of Orange Pond to 23300 mg kg^{-1} at the base of Eggtimer Pond. Concentrations of Mg ranged from 34.7 mg kg^{-1} to 1640 mg kg^{-1}, K from 25.2 mg kg^{-1} to 650 mg kg^{-1} and Ca from <1 mg kg^{-1} to 1720 mg kg^{-1}. Cl was the dominant anion followed by SO_4 and then HCO_3. Concentrations of Cl ranged from 847 mg kg^{-1} in Huey Pond to 36900 mg kg^{-1} at the base of Eggtimer Pond. Concentrations of SO_4 ranged from 151 mg kg^{-1} to 10000 mg kg^{-1} and HCO_3 ranged from 66 mg kg^{-1} to 5610 mg kg^{-1}. Changes in major ion concentrations with depth are shown for the stratified meltwater ponds in Figure 4.4 and in the two mixed ponds in Figure 4.5.

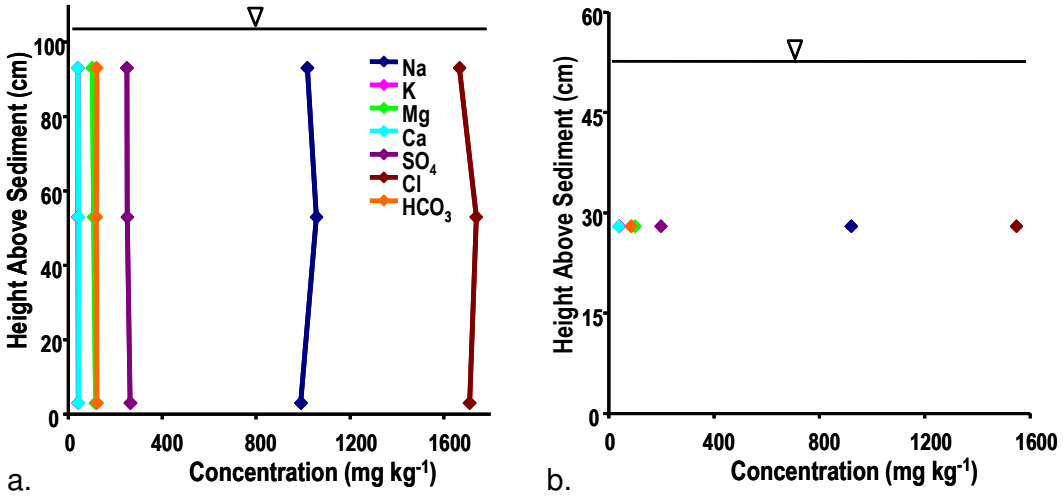

Figure 4.5 Major ion concentrations with depth in two, fully melted, mixed Bratina Island meltwater ponds (a. P70 Pond; b. Huey Pond) in January 2007. The horizontal line and inverted triangle symbol indicate water level at time of sampling.

4.3.3 Geochemistry of Ponds during the Dynamic Freezing Phase

Measurements of the physical characteristics of meltwater ponds during the dynamic freezing phase were recorded repeatedly in four Bratina Island meltwater ponds between February 2008 and April 2008. These four ponds were P70 Pond, Orange Pond, Egg(timer) Pond (see note following) and Skua Pond. The pond previously referred to as Eggtimer Pond had dropped in water level to form two discrete ponds – Egg and Timer. References made to this pond from the 2008 season will use the nomenclature Egg(timer) Pond to avoid confusion with earlier sampling periods when the pond was in its combined state. The physical characteristics of the four meltwater ponds are presented in full in Appendix 2.

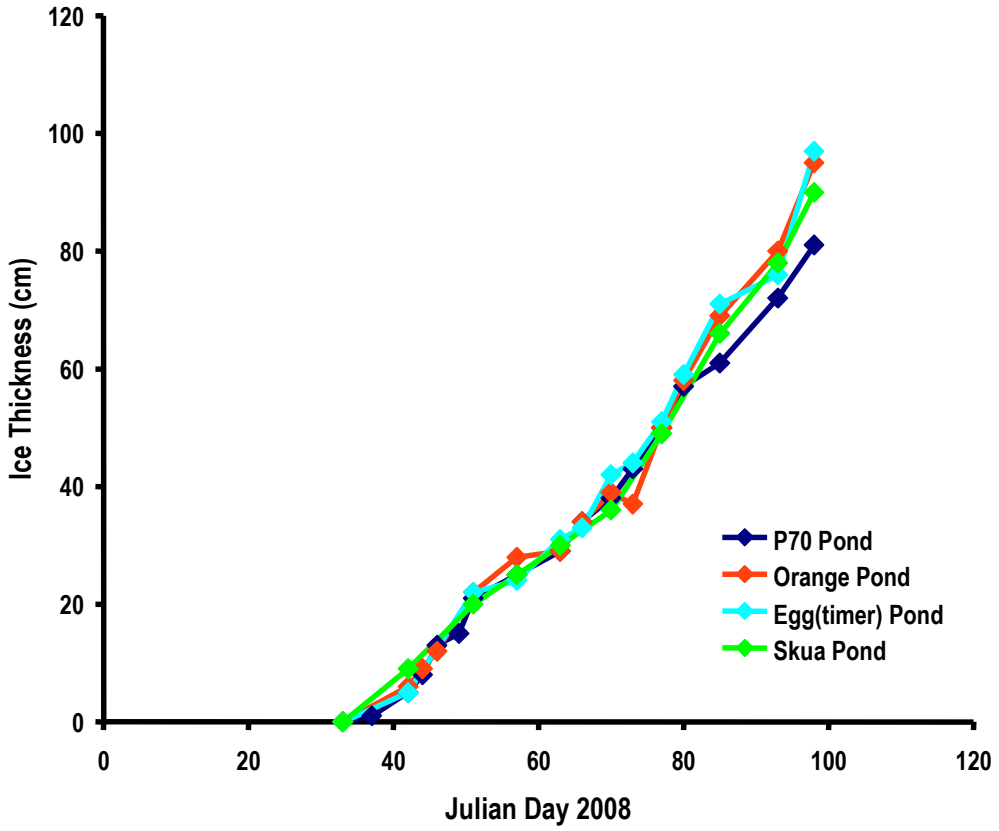

Figure 4.6 Increasing surface ice thickness in four Bratina Island meltwater ponds over time in 2008 (from Julian day 33 to 98 or from 2nd February to 7th April).

The temperature of the ponds ranged from a high of 6.1˚C in February (in P70 Pond) to a low of -2.7 ˚C in early April (in Egg(timer) Pond) illustrating the progressive cooling that took place during this period. Figure 4.6 shows the minimum temperatures in the four ponds decreasing over time. The thickness of ice that formed at the surface of each pond during the sampling period is given in Figure 4.6. The average ice growth rate was 1.23 cm day^{-1} in P70 Pond, 1.44 cm day^{-1} in Orange Pond, 1.47 cm day^{-1} in Egg(timer) Pond and 1.36 cm day^{-1} in Skua Pond. With

increasing ice thickness (see Figure 4.6) the electrical conductivity of the residual water phase increased from 5.27 mS cm^{-1} to 46.4 mS cm^{-1} in P70 Pond, from 0.54 mS cm^{-1} to 40.7 mS cm^{-1} in Orange Pond, from 4.3 mS cm^{-1} to 63.8 mS cm^{-1} in Egg(timer) Pond, and from 1.05 mS cm^{-1} to 9.33 mS cm^{-1} in Skua Pond. The minimum and maximum conductivities in each the four ponds over time are shown in Figure 4.7, with maximums generally occurring in the basal layer of the pond. Dissolved oxygen remained in the ponds through out the period but decreased gradually during the study period (Figure 4.8). Concentrations were measurable in all four ponds for the entire measurement period. A pronounced peak in dissolved oxygen was measured in P70 Pond on the 20th February with concentrations reaching 161 mg L^{-1}.

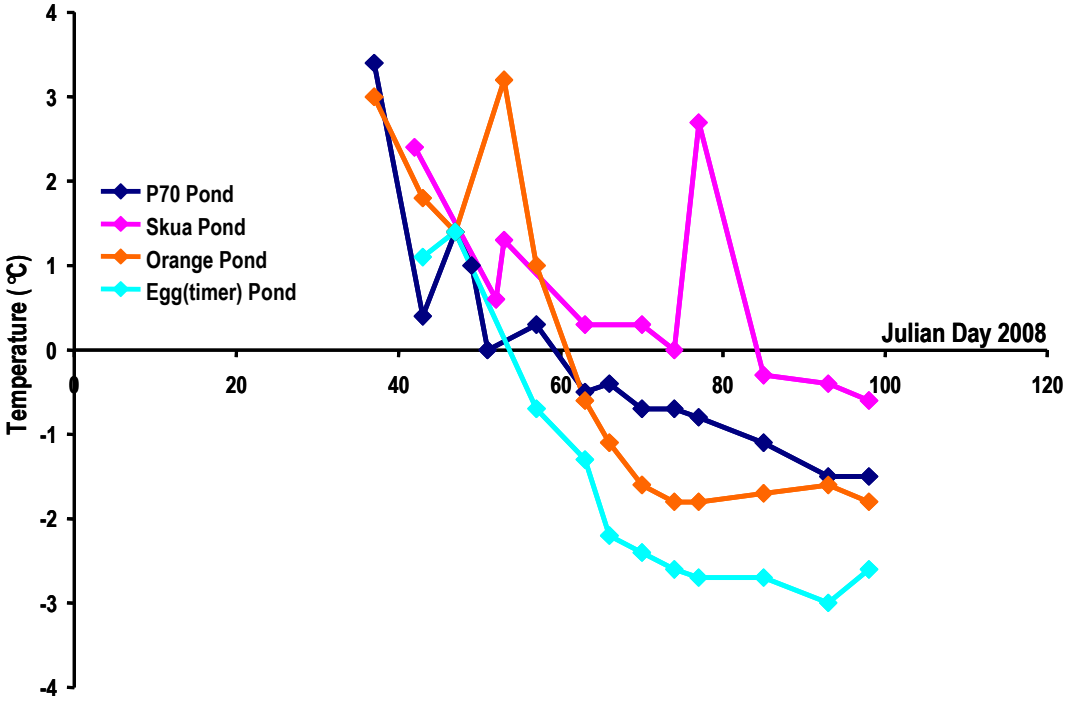

Figure 4.7 Minimum temperatures recorded in four meltwater ponds during progressive freezing over time.

Concentrations of major ions in the four dynamic ponds, Egg(timer) Pond, P70 Pond, Orange Pond and Skua Pond, over time are presented in Table 4.6, 4.7, 4.8 and 4.9 below. Major ion concentrations at the base of each of these four ponds at each repeat sampling are shown in Figures 4.9, 4.10, 4.11 and 4.12 showing the change in basal brine composition over time.

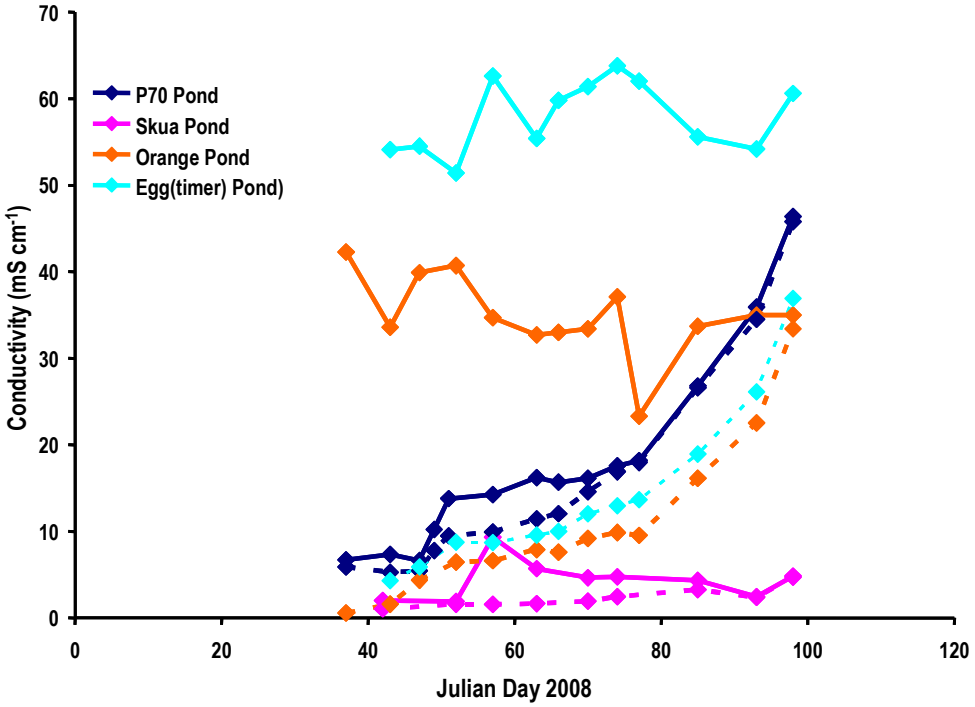

Figure 4.8 Minimum (dashed lines) and maximum (solid lines) electrical conductivities recorded in four meltwater ponds during progressive freezing over time. Maximum values predominantly occurred in the basal water layer of the pond.

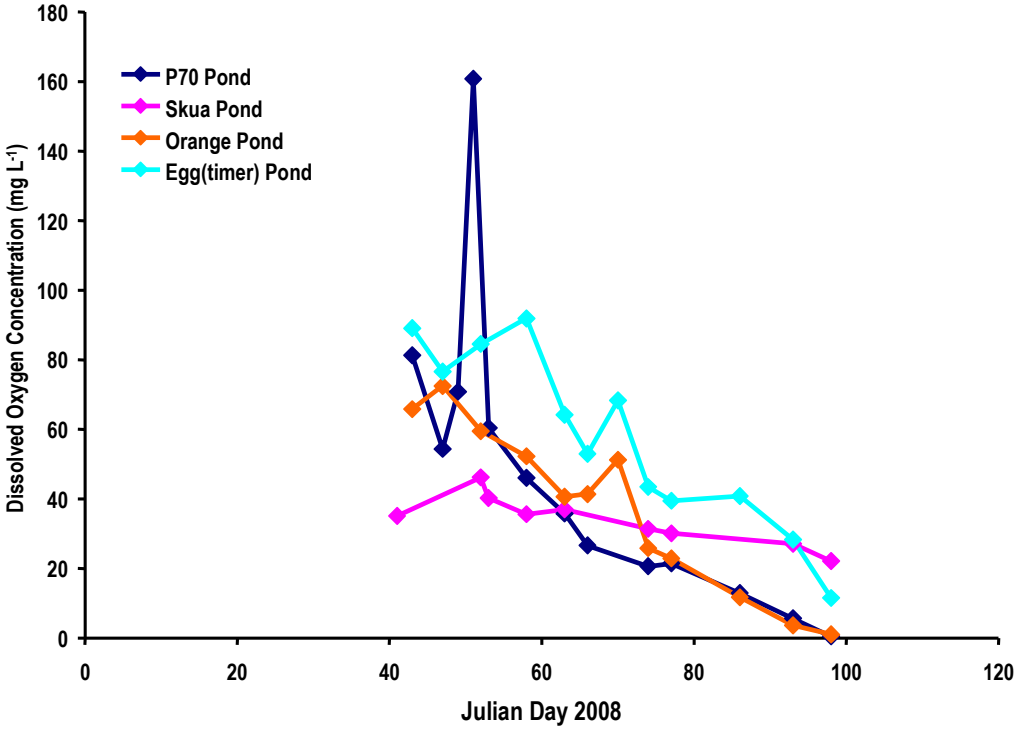

Figure 4.9 Maximum dissolved oxygen concentrations recorded in four meltwater ponds during progressive freezing over time.

Table 4.6 Major Ion Concentrations in (Egg)timer Pond with depth between 4 February 2008 and 28 March 2008.

Sampling Date	Height Above Sediment	Na	K	Mg	Ca	Cl	SO_4	HCO_3
	cm	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
4-Feb-08	110	1130	38.2	190	21.1	1720	193	257
	30	5460	179	1070	29.5	9430	1030	899*
5-Feb-08	118	1010	39.5	179	20.6	1700	147	334
	108	962	38.7	184	21.2	1760	183	330
	98	961	36.8	164	21.3	1770	181	290
	88	987	39.6	188	21.6	1800	183	327
	78	956	38.7	179	21.4	1620	152	305
	68	858	41.4	176	21.3	1630	178	286
	58	889	37.2	183	20.9	1830	181	301
	48	916	40.4	188	20.4	1690	180	338
	38	894	40.1	187	21.7	1770	190	338
	28	865	47.4	215	22.8	2050	208	446
	18	5830	225	1330	40.5	13200	1470	1140*
4-Mar-08	95	1550	61.9	170	32.7	2480	267	431
	85	1817	75.2	188	20.2	3040	345	428
	75	1960	74.4	191	22.2	2880	327	425
	65	1720	68.4	184	25.4	2770	315	420
	55	1920	74.7	193	22.6	3240	342	414
	45	1750	74.9	188	21.8	3070	323	420
	35	2060	75.5	187	20.7	3950	327	425
	25	2070	83.6	198	26.1	3570	376	420
	15	5080	149	203	18.0	8750	1040	760*
28-Mar-08	62	4060	149	531	52.7	6430	703	824
	52	4090	149	539	53.1	7800	837	799
	42	4040	147	530	47.7	6720	683	793
	32	4260	147	553	41.4	6340	752	891
	22	5010	156	665	26.8	8060	1010	848*
	12	8440	204	1070	32.6	15300	2140	1260
	2	12800	256	1570	48.4	22400	3300	2120*

*Although SO_4 appears more dominant than HCO_3 when compared on a weight basis, the reverse is true on a molar basis

Both Eggtimer and Orange Pond had significant concentrations of HCO_3 in the residual brine (2120 mg kg^{-1} and 3050 mg kg^{-1} respectively) although this was notably less than concentrations in the summer (January 2007) basal brines (5610 mg kg^{-1} and 5780 mg kg^{-1} respectively).

Concentrations of HCO_3 in the residual brine of P70 Pond (409 mg kg^{-1}) and Skua Pond (417 mg kg^{-1}) were an order of magnitude lower than the other ponds sampled. P70 Pond and Orange Pond had similar cation concentrations with differing anion compositions (P70 Pond had relatively more Cl and less HCO_3 ions and visa versa in Orange Pond).

The major ion composition of Egg(timer) Pond was dominated by the Na cation and the Cl anion. Magnesium was the second dominant cation followed by K and Ca. Concentrations of HCO_3 exceeded SO_4 in all but one sample (12 cm above the base of the pond, 28 March 2008). The concentration range for each of the major ions were 856 – 12800 mg kg^{-1} of Na, 36.8 – 256 mg kg^{-1} of K, 164 – 1570 mg kg^{-1} of Mg, 18 – 48.4 mg kg^{-1} of Ca, 1615 – 22400 mg kg^{-1} of Cl, 147 – 3300 mg kg^{-1} of SO_4 and 257 – 2120 mg kg^{-1} of HCO_3. The concentrations of major ions in the basal brine (Figure 4.9) showed a slight decrease between early February samples and early March samples, then increased at the end of March.

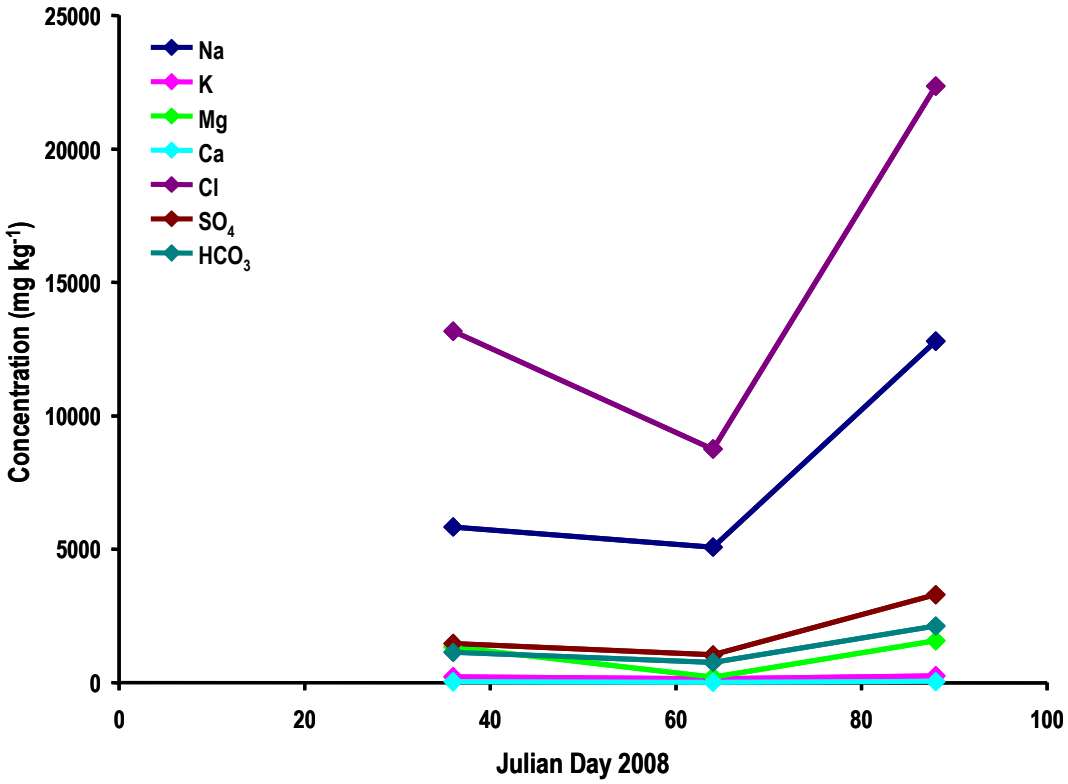

Figure 4.10 Concentrations of major ions at the base of Egg(timer) Pond over time (between 05.02.08 and 28.03.08) during progressive freezing from the pond surface downwards.

The major ion composition of Orange Pond was dominated by the Na cation and the Cl anion. Magnesium was the second dominant cation followed by K and Ca. Concentrations of HCO_3

exceeded SO_4 in all samples except the base of the pond in late January when the reverse was true. The concentration range for each of the major ions were 700 - 8370 mg kg^{-1} of Na, 35.2 - 254 mg kg^{-1} of K, 48.6 - 359 mg kg^{-1} of Mg, 1.66 – 8.35 mg kg^{-1} of Ca, 1030 - 10100 mg kg^{-1} of Cl, 151 - 1840 mg kg^{-1} of SO_4 and 165 - 3050 mg kg^{-1} of HCO_3. The concentrations of major ions in the basal brine (Figure 4.10) showed a slight decrease between early February samples and early March samples (with the exception of Na which showed a steady increase), then increased at the end of March.

Table 4.7 Major Ion Concentrations in Orange Pond with depth between 25 January 2008 and 29 March 2008.

Sampling Date	Height Above Sediment	Na	K	Mg	Ca	Cl	SO_4	HCO_3
	cm	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
25-Jan-08	105	739	36.1	49.7	8.35	1030	152	165
	65	700	35.3	48.6	8.07	1030	151	213
	15	14000	598	178	6.20	18200	2680	799
13-Feb-08	95	1050	42.2	84.3	5.35	1510	218	703
	55	1020	44.7	76.3	4.90	1550	206	694
	15	4180	290	410	7.01	8780	1160	-
4-Mar-08	65	1840	78.0	78.8	3.2	2270	308	646
	45	1730	80.5	75.8	3.5	2200	321	642
	5	5620	186	148	4.9	7010	1130	2110
29-Mar-08	55	4390	190	270	2.33	6330	896	1670
	45	4340	186	273	3.35	6540	851	1730
	30	4440	181	234	1.66	6870	886	1610
	20	5680	194	259	5.78	7740	953	1680
	15	7400	232	294	3.68	9220	1530	2450
	10	8370	254	359	3.74	10100	1840	3050

The major ion composition of P70 Pond was dominated by the Na cation and the Cl anion. Magnesium was the second most dominant cation followed by K and Ca. Concentrations of HCO_3 exceeded SO_4 in all samples. The concentration range for each of the major ions were 839 - 8770 mg kg^{-1} of Na, 43.2 - 254 mg kg^{-1} of K, 97.1 - 967 mg kg^{-1} of Mg, 36.0 – 91.4 mg kg^{-1} of Ca, 1760 - 13400 mg kg^{-1} of Cl, 259 - 2110 mg kg^{-1} of SO_4 and 31.2 - 409 mg kg^{-1} of HCO_3. The concentrations of major ions in the basal brine (Figure 4.11) showed a steady increase in concentration over time.

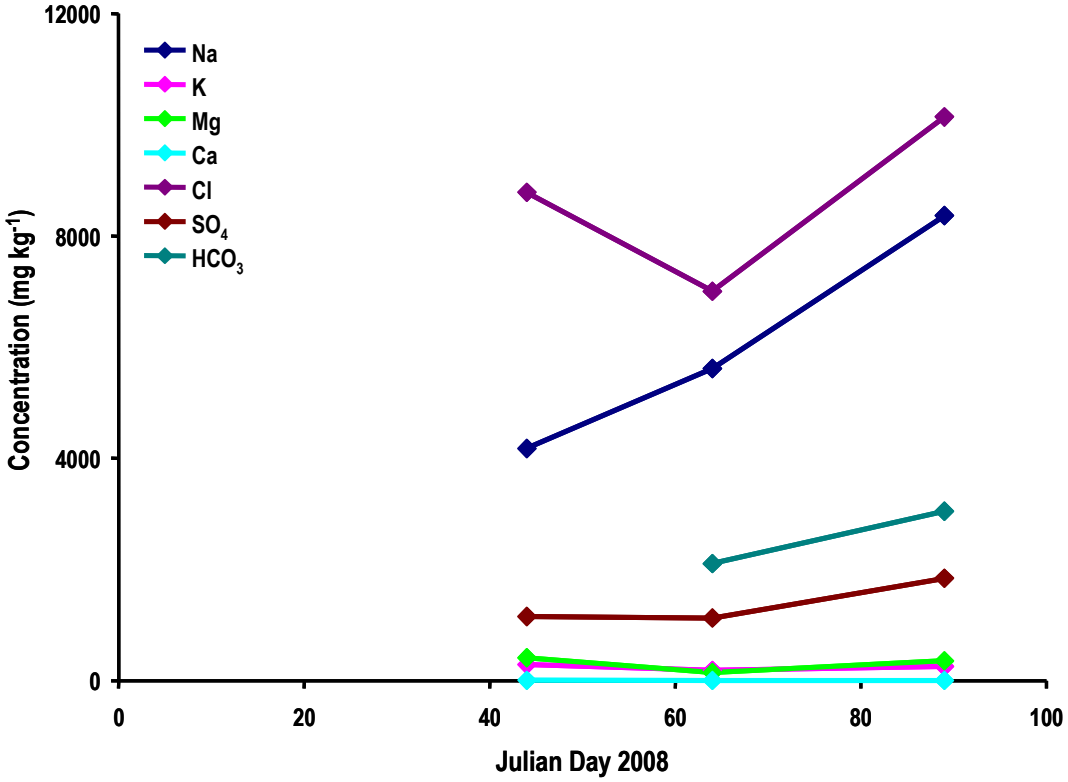

Figure 4.11 Concentrations of major ions at the base of Orange Pond over time (between 13.02.08 and 29.03.08) during progressive freezing from the pond surface downwards.

Table 4.8 Major Ion Concentrations in P70 Pond with depth between 25 January 2008 and 4 April 2008.

Sampling Date	Height Above Sediment	Na	K	Mg	Ca	Cl	SO_4	HCO_3
	(cm)	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
25 Jan-08	90	1060	48.5	98.9	46.6	1760	259	68.9
	60	1060	48.8	97.5	46.0	1820	314	69.5
	20	1060	49.8	97.1	46.4	1780	263	75.1
7-Feb-08	95	883	43.2	179	37.6	2040	297	67.1
	65	849	46.4	160	36.0	2060	300	73.2
	25	839	48.3	166	36.1	2070	300	73.2
19-Feb-08	65	1770	67.8	163	38.9	3300	476	48.2
	25	1740	67.9	163	38.8	3400	539	31.2
4-Mar-08	67	2410	93.4	186	61.0	3930	585	70.2
	27	2470	91.2	178	55.3	3790	570	69.5
18-Mar-08	51	4050	148	396	71.0	7490	1050	239
	26	3960	149	398	76.8	6670	907	252
4-Apr-08	10	8770	254	967	91.4	13400	2110	409

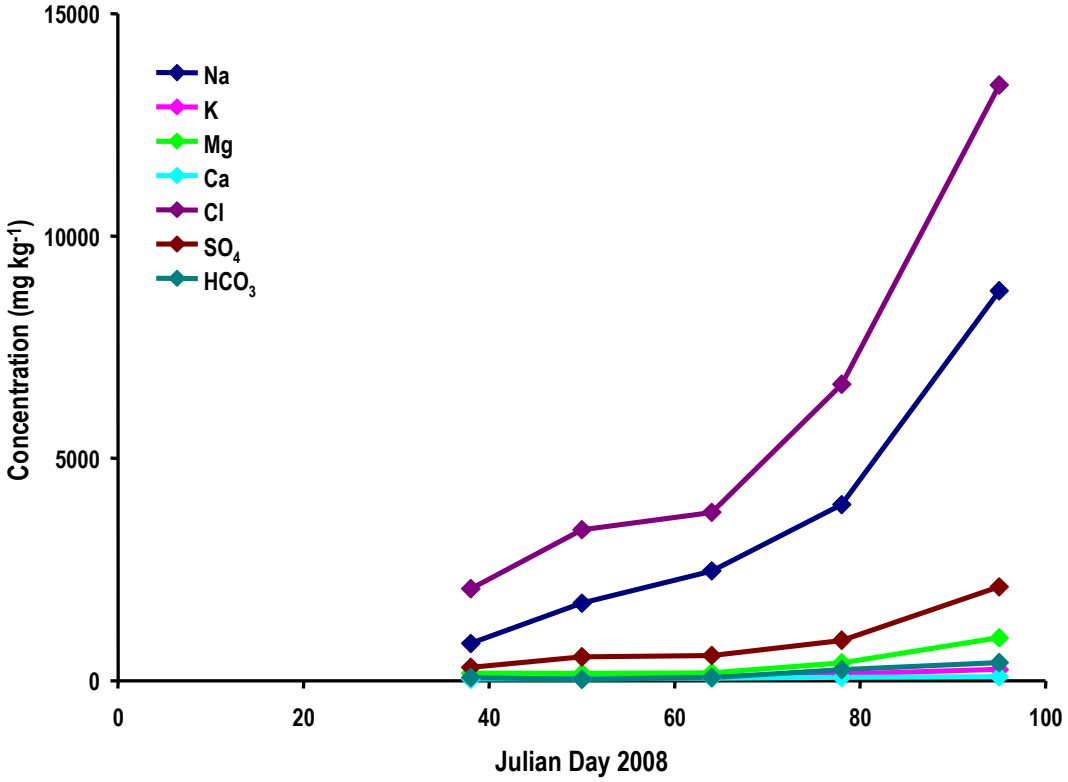

Figure 4.12 Concentrations of major ions at the base of P70 Pond over time (between 07.02.08 and 04.04.08) during progressive freezing from the pond surface downwards.

Table 4.9 Major Ion Concentrations in Skua Pond with depth between 7 February 2008 and 27 March 2008.

Sampling Date	Height Above Sediment	Na	K	Mg	Ca	Cl	SO_4	HCO_3
	(cm)	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
7-Feb-08	120	248	6.9	19.2	13.0	194	311*	144
	80	239	9.0	17.0	12.9	190	309*	145
	20	272	10.0	17.7	16.1	214	358*	192
4-Mar-08	100	324	12.5	21.0	16.3	332	436*	103
	85	305	12.7	20.8	21.9	271	446*	95.0
	25	434	17.3	19.6	22.3	300	520*	104
27-Mar-08	75	875	28.5	55.9	40.1	680	1070*	323
	35	847	27.1	52.1	37.6	663	1070*	320
	5	1160	34.8	57.6	40.1	748	1650*	417

*Although SO_4 appears more dominant than Cl when compared on a weight basis, the reverse is true on a molar basis

The major ion composition of Skua Pond was dominated by the Na cation and the Cl anion (although concentrations of SO_4 by weight exceed those of Cl). Magnesium was the second

dominant cation followed by Ca then K, in all samples except 25 cm and 85 cm above the sediment on 4th March when Ca slightly exceeded Mg. The concentration range for each of the major ions were 239 - 1160 mg kg^{-1} of Na, 6.9 – 34.8 mg kg^{-1} of K, 17.0 – 57.6 mg kg^{-1} of Mg, 12.9 – 40.1 mg kg^{-1} of Ca, 190 - 748 mg kg^{-1} of Cl, 309 - 1650 mg kg^{-1} of SO_4 and 95 - 417 mg kg^{-1} of HCO_3. The concentrations of major ions in the basal brine (Figure 4.12) showed a steady increase over time with the exception of HCO_3 which decreased by 88 mg kg^{-1} in the second sampling (4th March), before increasing in concentration at the end of March.

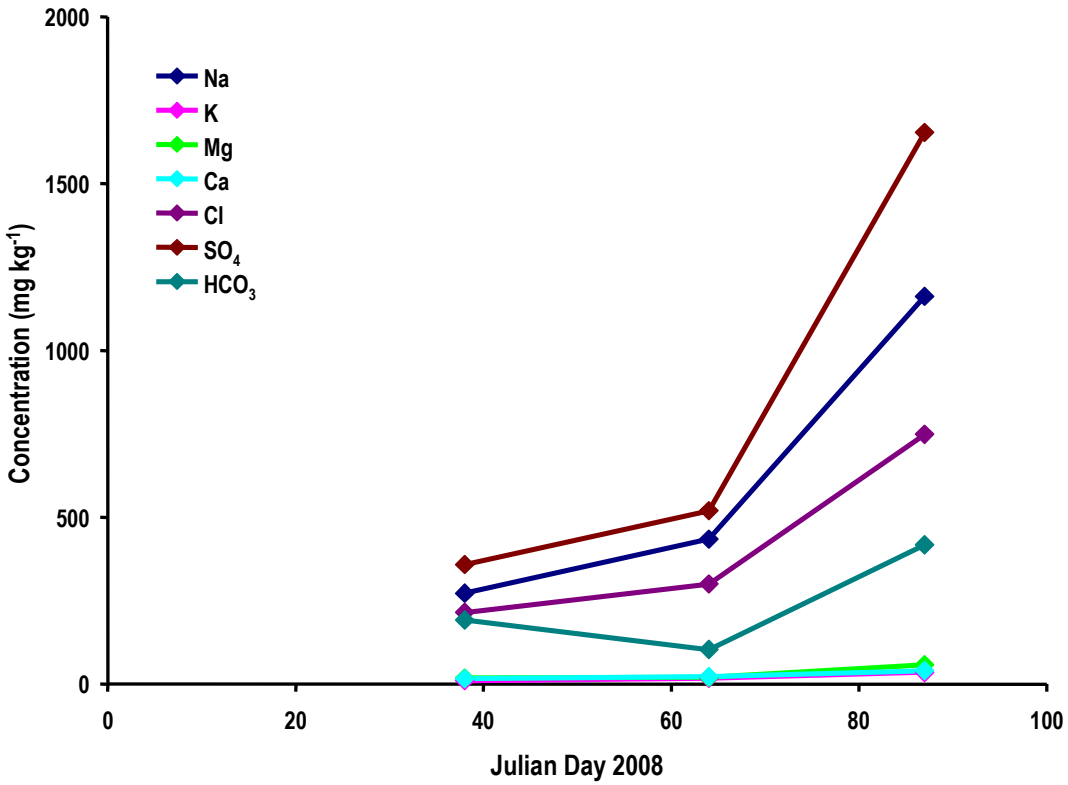

Figure 4.13 Concentrations of major ions at the base of Skua Pond over time (between 07.02.08 and 27.03.08) during progressive freezing from the pond surface downwards.

4.3.4 Salts Precipitated in or near Meltwater Ponds

Salt minerals identified in and around Bratina Island meltwater ponds identified included halite (NaCl), mirabilite ($Na_2SO_4.10H_2O$), thenardite (Na_2SO_4), magnesite ($MgCO_3$), gypsum ($CaSO_4$), sodium carbonate ($NaCO_3$) and calcite ($CaCO_3$). The presence of diatoms, silicates, cyanobacterial mat and sponge spicules was also noted. The term silicate is used in this instance as a general reference to any mineral that contained significant silicon and oxygen (SiO_2) and was not identified further. Silicates make up the majority of rock forming minerals on Earth and are ubiquitous on the surface of the MIS.

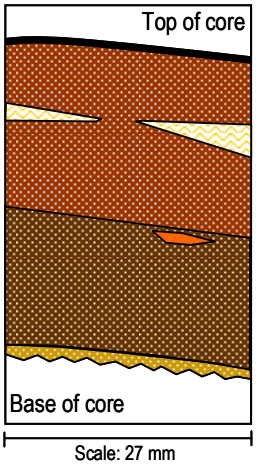

Figure 4.14 Schematic of a sediment core from P70E Pond taken adjacent to the top of the basal brine layer. A layer of cyanobacteria was present at the top of the core (thick black line) above three horizons of differently coloured sandy material. A lens of crystalline gypsum (yellow) was present near the top of the core.

From several cores collected from sediments near the top of the brine layer in P70E Pond it was found that salt precipitates were dominated by gypsum with significant amounts of calcite and halite. All three salts were present on the surface and underside of the cyanobacterial mat layer that would have been adjacent to the pond water. Diatoms were also present and a Ti-Fe mineral was also identified on the underside of the mat layer. The sediment matrix primarily contained the salt gypsum and silicates and the lighter sediment layer in these cores also contained a significant number of diatoms. Unique to the P70E sediment samples were the presence of several lenses of crystalline gypsum that was easily visible to the naked eye (Figure 4.14).

In Upper Pond a sediment core collected from the near the pond edge (in approximately 20 cm water depth) revealed no salt precipitates instead being dominated by silicate minerals and a few diatoms. Conversely, sediment cores taken from the base of the pond from within the brine layer contained mirabilite and thenardite (as evidenced by their differing habits), magnesite, $NaCO_3$,

calcite and, on the surface of the mat only, halite. Interestingly, no gypsum was identified in Upper Pond. As in P70E Pond, the sandy matrix was made up of silicates with some diatoms.

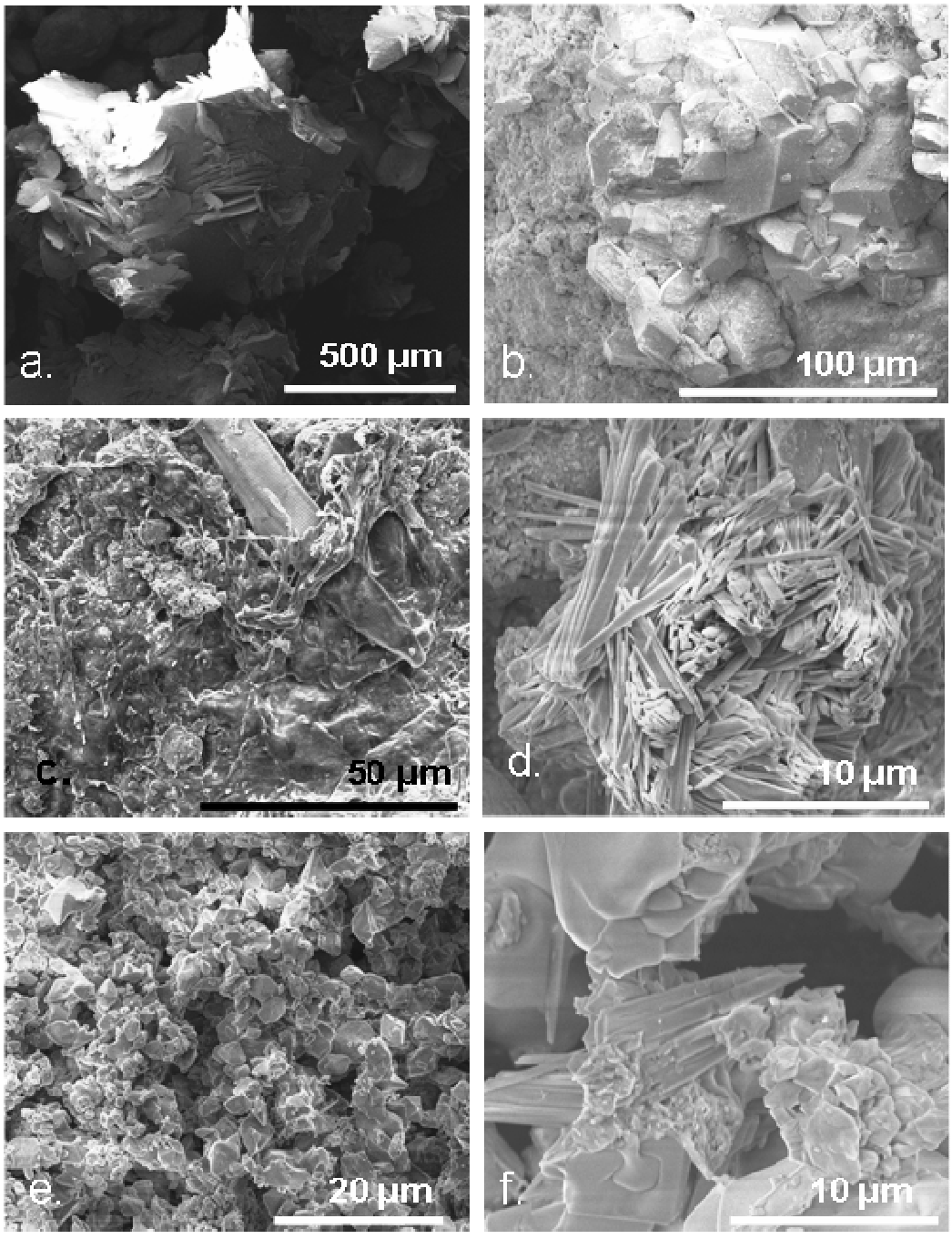

Figure 4.15 SEM images from in and around meltwater ponds a. large plated gypsum, b. euhedral prismatic gypsum, c. typical microbial mat surface with diatom, d. acicular mirabilite, e. small dipyrimidal thenardite, and f. mirabilite (acicular) and thenardite (blocky) with larger NaCl crystals.

Cyanobacterial mat collected from Marlin Pond, a newly re-saturated pond outside the usual field area, had several salt precipitates associated with it. On the surface of the mat thenardite dominated while mirabilite and gypsum were both present. The underside of the mat showed

halite and calcite, and not surprisingly a cross-section of the mat showed a mixture of all five minerals. A background scan using the SEM revealed very high concentrations of Ca in the sample in keeping with the presence of calcite and gypsum.

Samples collected from areas surrounding ponds were dominated by thenardite and halite with lesser amounts of mirabilite, gypsum and Na, Ca and Mg carbonates. The white salt rinds coating the underside of gravels revealed either halite or thenardite while visible soil salts tended to be thenardite with sodium carbonate, magnesite, gypsum and calcite. Rock fragments and silicate minerals were also present. All salts that were identified within ponds were also identified in the surrounding sediments.

The two varieties of sodium sulfate, mirabilite and thenardite, were distinguishable by their differing habit. Mirabilite formed acicular (needle-like) or bladed crystals, often occurring in clusters while thenardite crystals were tabular or dipyramidal. The anhydrous thenardite may be an artefact of hydrous mirabilite drying. Mineral habits are shown in Figure 4.15.

4.4 Discussion 1: Geochemical Variation in Meltwater Ponds

4.4.1 Physical Properties of Meltwater Ponds during Summer Thaw

In general, the meltwater ponds sampled mid summer (i.e. January 2007 samples) were warmer (temperatures of 4.2 – 11.9˚C compared to 3.5 – 9.4˚C) and more alkaline (a pH range of 8.03 – 10.69 compared to 7.95 – 9.44) than when sampled immediately post melting. Meltwater pond temperatures reflect the increase in solar radiation that warms the ponds over time, while the increase in pH appears to be biologically driven by the metabolic uptake and fixation of dissolved CO_2 by cyanobacteria during photosynthesis (Chapter 7). Dissolved oxygen showed the most variation in the 2005 samples, ranging from 1 mg L^{-1} to >20 mg L^{-1} in the basal brine, however by late January 2007, the ponds tended to be at or slightly exceeding 100% saturation throughout the water column. The shift from an anoxic to an oxic environment in the basal brine as the ice plug melts away most likely reflects the commencement of photoautotrophic processes (that release oxygen) in the ponds which continue through the summer melt period.

The thickness of the high conductivity basal brine layer varied between ponds but ranged from <5 cm above the base of the pond (P70 Pond and Orange Pond) to 27 cm above the base of the pond (Upper Pond). Conductivity ranged from 4.17 mS cm^{-1} at the surface of Huey Pond to 74 mS cm^{-1} at the base of P70 Pond in 2005 with the greatest conductivity range (of 69.2 mS cm^{-1}) recorded in P70 Pond. When the ponds were fully melted (late January 2007), conductivity ranged from 2.1 mS cm^{-1} at the surface of Orange Pond to 64.1 mS cm^{-1} at the base of Eggtimer

Pond with the greatest conductivity range (of 61.6 mS cm^{-1}) recorded in Eggtimer Pond. No overall decrease in basal brine thickness or conductivity was observed as the summer melt period progressed.

4.4.2 Variation in the Composition of Meltwater Ponds during Summer Thaw

Compositional variation between Bratina Island ponds, despite their close spatial proximity (see pond location map in Figure 2.2), is illustrated in the ternary diagrams in Figure 4.16 and Figure 4.17. The four study ponds were all dominated by Na and Cl ions, when sampled immediately post melting in December 2005. In 2007, the meltwater ponds remained Na-Cl dominated with none of the Na-SO_4 dominated waters that have been previously reported (e.g. Wait *et al.* 2006), despite samples being collected from several of the same ponds.

Spatial variation in composition between ponds most likely reflects differences in the minerals precipitated out of the water column within each pond over time. P70E Pond was the most Cl dominant pond (>95 % Cl) and Upper Pond and Orange Pond were the least Cl dominant with relatively higher proportions of SO_4 (~14 – 22 %) and HCO_3 (~14 – 35 %) respectively. P70E and VXE6 Pond were the only ponds in which Na+K made up less than 87% of the cation composition. Although not adjacent ponds, the proportion of ions P70 Pond and Huey Pond were very similar to each other potentially indicating a similar evolutionary history and/or age. In 2007, Eggtimer Pond also has very similar compositional characteristics to these ponds, despite being stratified with high conductivity basal brine.

Temporal changes in the chemical composition of meltwater ponds occur in individual ponds at different stages during summer from immediately post melting (December 2005) to mid summer (January 2007). Temporal variation in the composition of the meltwater ponds in 2005 and 2007 and the can be seen in the ternary diagrams in Figure 4.16 and Figure 4.17 respectively. In general, the compositional characteristics of each individual pond did not vary significantly between 2005 and 2007, despite concentration changes with depth.

The composition of water in the lower water column of stratified meltwater ponds reflects the composition of the pond towards the end of freezing during the previous winter as the brine layer had not completely remixed. Upper Pond, VXE6 Pond and Orange Pond showed the greatest compositional variation with depth with the non-linear concentration variation observed in the basal brine suggesting that mineral precipitation or dissolution processes were also in effect at the later stages of freezing. The upper (mixed) water layers showed linear compositional change indicative of a straightforward concentration gradient.

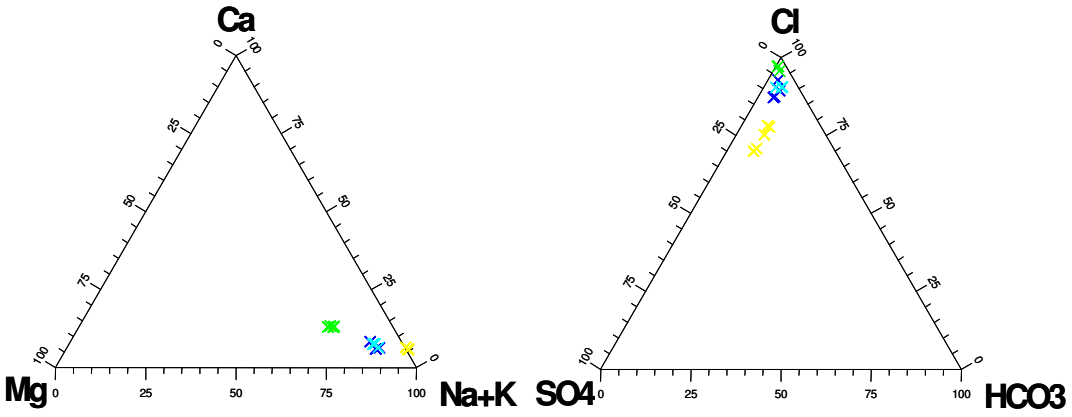

Figure 4.16 Ternary diagram for Bratina Island meltwater pond cations (a.) and anions (b.) in December 05 (molar concentrations). Upper Pond – yellow; Huey Pond – bright blue; P70 Pond – light blue and P70E Pond – green.

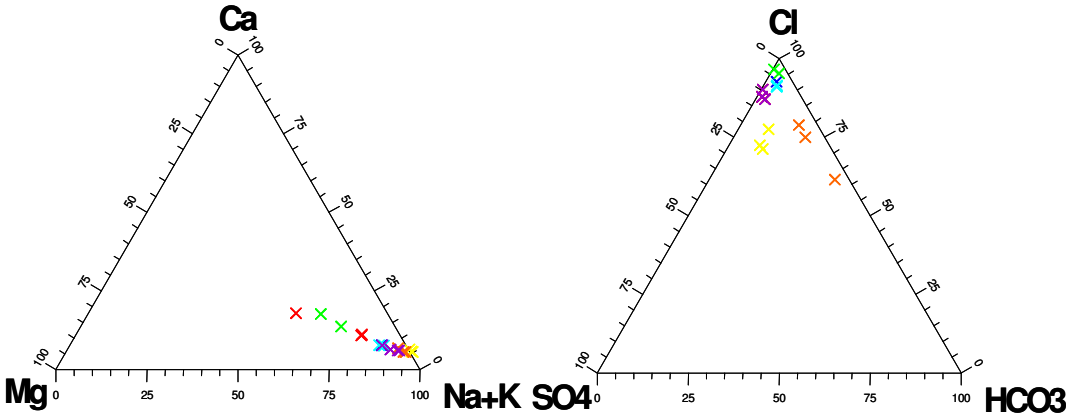

Figure 4.17 Ternary diagram for Bratina Island meltwater pond cations (a.) and anions (b.) in January 07 (molar concentrations). Upper Pond – yellow; Huey Pond – bright blue; P70 Pond – light blue; P70E Pond – green; Orange Pond – orange; VXE6 – red and Eggtimer Pond – purple.

The ponds that retained stratification in both 2005 and 2007 were Upper Pond and P70E Pond. The proportion of cations in Upper pond basal brine show virtually no change between 2005 and 2007 although Cl decreased from 77 to 72 % and SO_4 increased from 14 to 19 %. However concentrations of Na and SO_4 increased during this period (from 11700 mg kg^{-1} to 14200 mg kg^{-1}, and from 6500 mg kg^{-1} to 10000 mg kg^{-1} respectively) while Cl showed relatively little concentration change. This proportional increase and concentration increase in SO_4 is strongly indicative of SO_4 mineral dissolution into the 2007 water column. Given that the concentration of Na also increased this is likely to be the dissolution of a Na-SO_4 mineral such as mirabilite. The proportion of cations and anions in P70E pond basal brine was similar between 2005 and 2007 however concentrations of ions were significantly lower in 2007 compared to 2005. For example, the concentration of Na and Cl in the basal brine in P70E Pond decreased from 12000 mg kg^{-1} to 5785 mg kg^{-1} and from 28616 mg kg^{-1} to 12876 mg kg^{-1} respectively. Given that all major ions decreased in concentration in the basal brine between 2005 and 2007, and that conductivity also

decreased, this most likely reflects partial diffusion or mixing of the basal brine into the overlying water column.

4.4.3 Variation in the Composition of Meltwater Ponds during Freezing

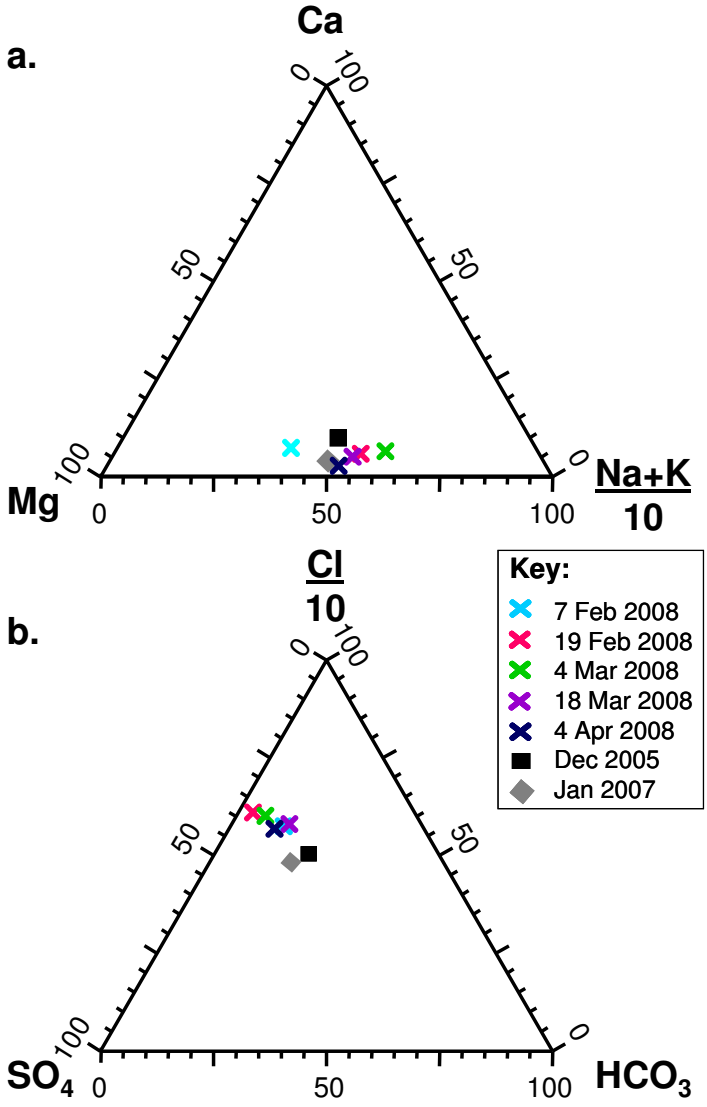

Figure 4.18 Ternary diagrams showing basal water composition in P70 Pond in December 2005 and January 2007 when the pond was fully melted and at various stages of freezing in March/April 2008; a) cations and b) anions.

Three of the four ponds repeatedly sampled in 2008 during freezing were Na-Cl dominated (Egg(timer) Pond, Orange Pond and P70 Pond) and only Skua Pond was Na-SO_4 dominated. In order to illustrate the similarities and differences between the cation and anion compositions of these meltwater ponds, ternary diagrams showing the dynamic basal brine composition over time are presented in Figures 4.18 to 4.21. The composition of basal brines collected in January 2007 and December 2005 are also illustrated for comparison. These diagrams allow the relative

composition of the ponds at different stages of freeze and thaw to be compared. In P70 Pond, anion compositions during freezing were more similar (marginally) to January 2007 basal brine compositions but were lower in HCO_3 than the summer samples (Figure 4.18b). The cation composition of P70 basal brines in December 2005, January 2007 and repeated samples in 2008 were all very similar with small differences in the relative proportion of Mg and Na+K (Figure 4.18a).

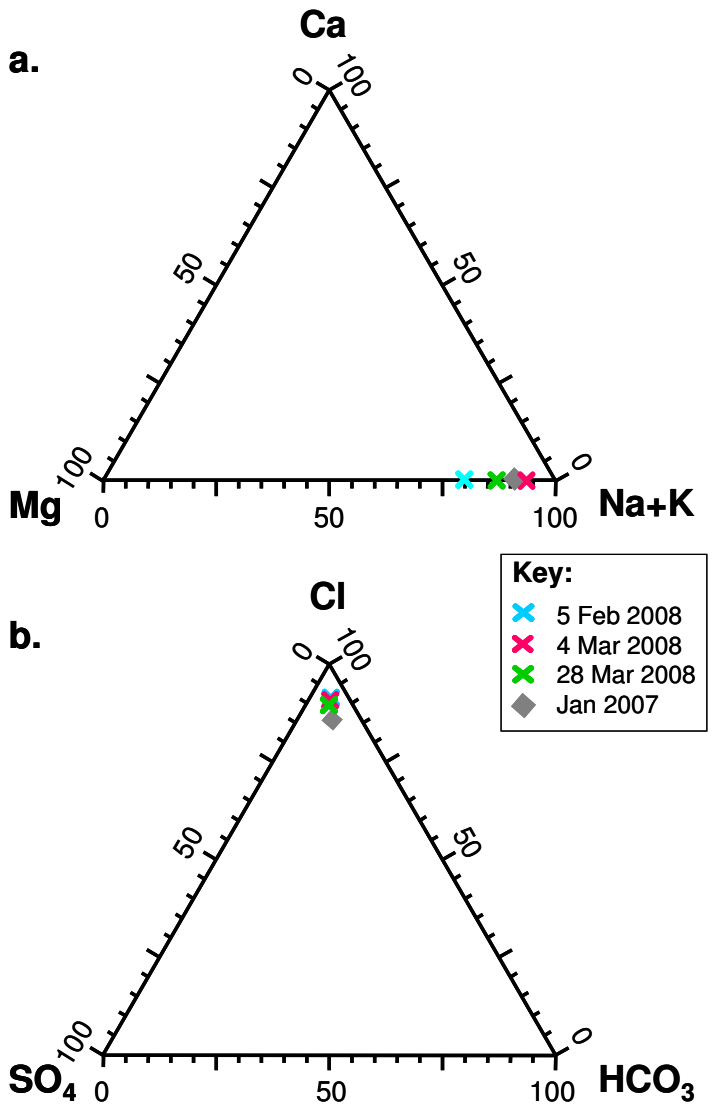

Figure 4.19 Ternary diagrams showing basal water composition in Eggtimer Pond in January 2007 when the pond was fully melted and Egg(timer) Pond at various stages of freezing in February/March 2008; a) cations and b) anions.

Of the four ponds sampled, Egg(timer) Pond had the highest concentration of major ions in the residual water phase at the end of the sampling period. The anion composition of basal brine during progressive freezing in this pond was very similar to that seen in the January 2007 basal

brine but with slightly more Cl, and less SO_4 and HCO_3 (Figure 4.19b). The cation composition of the brines sampled in 2008 spanned across the January 2007 sample with the later samples having relatively more Na+K and less Mg than earlier samples (Figure 4.19a).

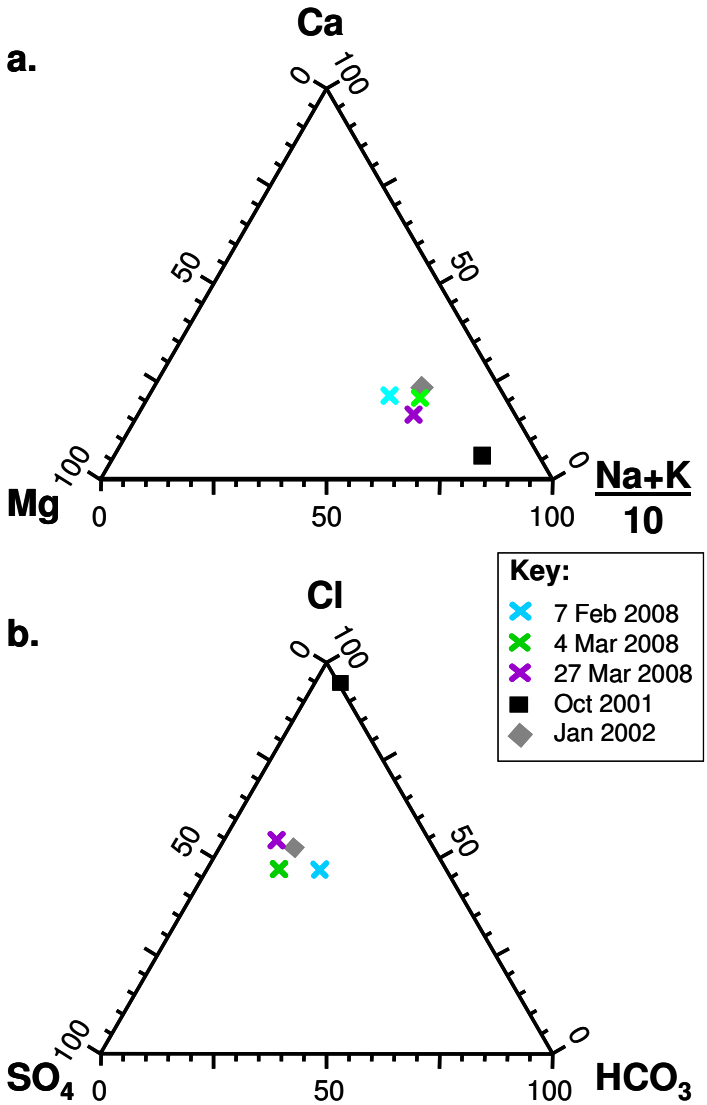

Figure 4.20 Ternary diagrams showing basal water composition in Skua Pond in October 2001 when all but the basal brine was fully frozen, in January 2002 when the pond was fully melted, and at various stages of freezing in February/March 2008; a) cations and b) anions.

As samples were not collected from Skua Pond during the 2005 and 2007 field seasons, basal brine compositions from October 2001 and January 2002 (data taken from Wait *et al.* 2006) were used for comparison. The cation composition of the 2008 samples was approximately halfway between the October 2001 and January 2002 samples. The close clustering of the samples indicates that the relative abundance of cations has not significantly changed over time despite significantly different sample conductivities (ranging from 1.28 mS cm^{-1} in January 2002 to 111 mS cm^{-1} in October 2001) (Figure 4.20a). Conversely, the relative abundance of anions in the

basal brines differed significantly between the sampling periods. Samples collected in 2008 were more similar to January 2002 basal brine (but with relatively less HCO_3) than the 2001 basal brine that was strongly dominated by the Cl ion (Figure 4.20b). In the 2002 and 2008 basal brines SO_4 was nearly equal in proportion to Cl.

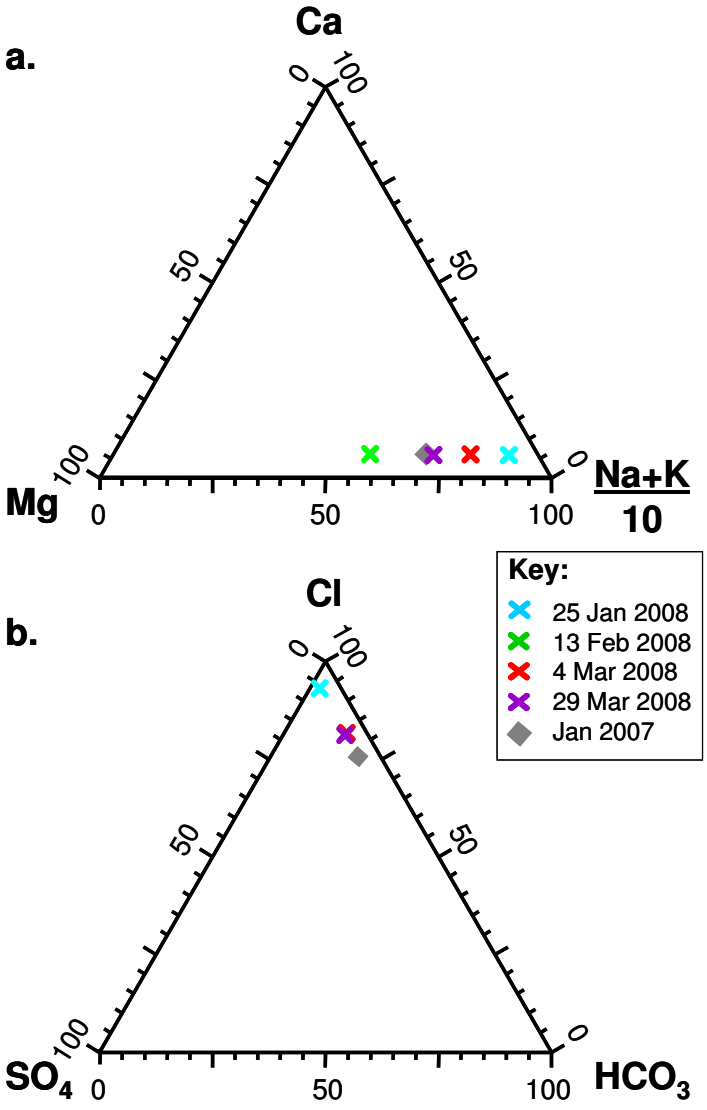

Figure 4.21 Ternary diagrams showing basal water composition in Orange Pond in January 2007 when the pond was fully melted and at various stages of freezing in March/April 2008; a) cations and b) anions.

The cation composition in the basal water of Orange Pond (Figure 4.21a) varied over time with Na+K becoming less then more dominant. This potentially reflects the mixing of a stratified water column beneath the growing ice cover by convection. The relative proportion of cations and anions (Figure 4.21b) in the final sample were very similar to proportions observed in the fully melted summer sample.

The composition differences between the four ponds during freezing, reflects the fully melted composition of the ponds during summer. The nature of the mineral precipitation that may occur during progressive freezing and the degree of biological activity occurring in the ponds appears to influence final brine compositions, as will be discussed in Section 4.5.

In general, the composition of the basal brines in dynamic meltwater ponds were more similar to January basal brines compared to those measured in December or earlier. The possible reason for the relative dissimilarity to the December 2005 samples is that when the ponds are newly melted the basal brine may be depleted in ions used for winter mineral precipitation. For example, the precipitation of mirabilite and gypsum would remove the SO_4 ion from solution making the residual basal brine relatively enriched in Cl. Similarly, the precipitation of carbonate bearing minerals (such as dolomite) would result in HCO_3 depletion in the basal brines until dissolution occurred. The relative depletion of HCO_3 in early thaw samples could also be the result of biological processes. This has important implications when determining the best time to collect samples for winter brine prediction.

4.4.4 Conservative vs. Non-Conservative Major Ion Concentrations

Chloride is usually assumed to behave conservatively in the environment due to the high solubility of the anion. This enables it to be used as an indication of the degree of concentration of the brine and the solubility of other ions can be assessed relative to Cl. The ratios of major cations and anions to Cl for each of the meltwater ponds sampled in December 2005 are shown graphically in Figure 4.22 and Figure 4.23 respectively. The same ratios are presented for January 2007 samples in Figure 4.24 and Figure 4.25.

In 2005 Na, K and Mg are all reasonably conservative with depth showing no significant deviation relative to Cl (Figure 4.22a-c). Calcium shows the least conservative behaviour with three of the four ponds decreasing in concentration relative to Cl at the base of the pond (Figure 4.22d). Only P70E showed no change in Ca:Cl with depth. Sulfate was generally conservative with depth relative to Cl, with the exception of Upper Pond which increased with depth in the upper water column then decreased in the basal brine (Figure 4.23a). Bicarbonate was also fairly conservative, but a slight decrease towards the base of the pond was seen in Huey Pond, P70E Pond and P70 Pond (Figure 4.23b).

In all ponds sampled in January 2007, the concentration of Na relative to Cl showed little change with depth indicating the conservative behaviour of the Na ion (Figure 4.24a). In Upper Pond and VXE6 Pond K was slightly lower in the basal brine compared to the overlying mixed water layer

(Figure 4.24b), and Mg decreased slightly in the basal brine in Eggtimer Pond (Figure 4.24c). In most of the stratified ponds Ca decreased relative to Cl in the basal brine with the exception of P70E Pond which showed an increase (Figure 4.24d). VXE6 Pond differed from the other ponds in that concentrations of K, Mg and Ca increased with depth in the upper water column to the top of the basal brine from which point concentrations decreased.

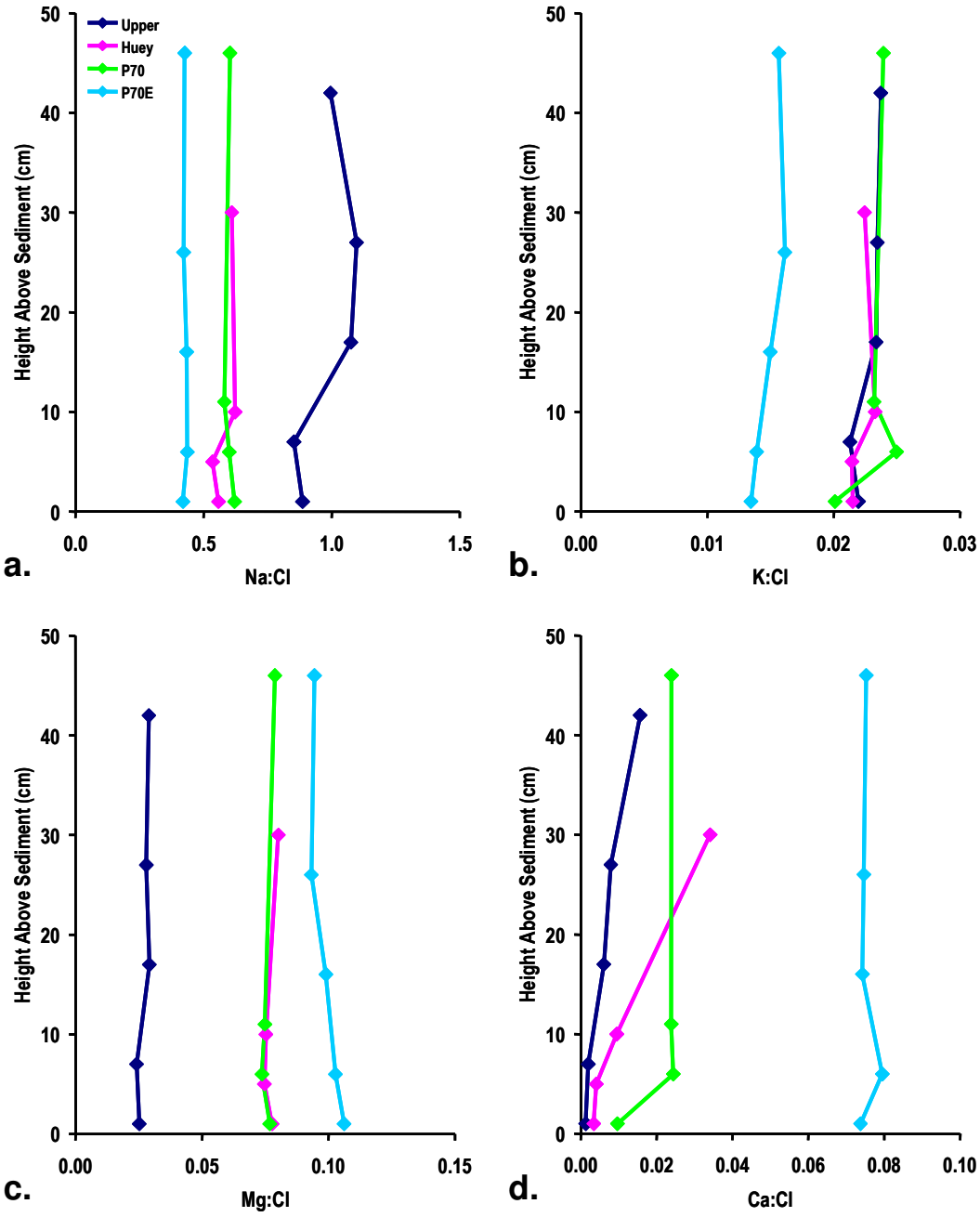

Figure 4.22 Graphs showing the ratio of major cations to Cl versus depth in four Bratina Island meltwater ponds in December 2005; a) Na, b) K, c) Mg and d) Ca.

Concentrations of SO_4 relative to Cl in 2007 were conservative with depth in most ponds but showed a slight increase in the basal brine of Eggtimer Pond and a slight decrease at the base of VXE6 Pond (Figure 4.25a). Upper pond decreased at the top of the basal brine layer before increasing at the very base of the pond. Concentrations of HCO_3 were generally conservative with depth; however, non-conservative behaviour was seen in Orange Pond where HCO_3 increased relative to Cl at the top of the basal brine layer before decreasing at the very base of the pond (Figure 4.25b). VXE6 Pond also showed a slight decrease in HCO_3 relative to Cl at the base of the pond.

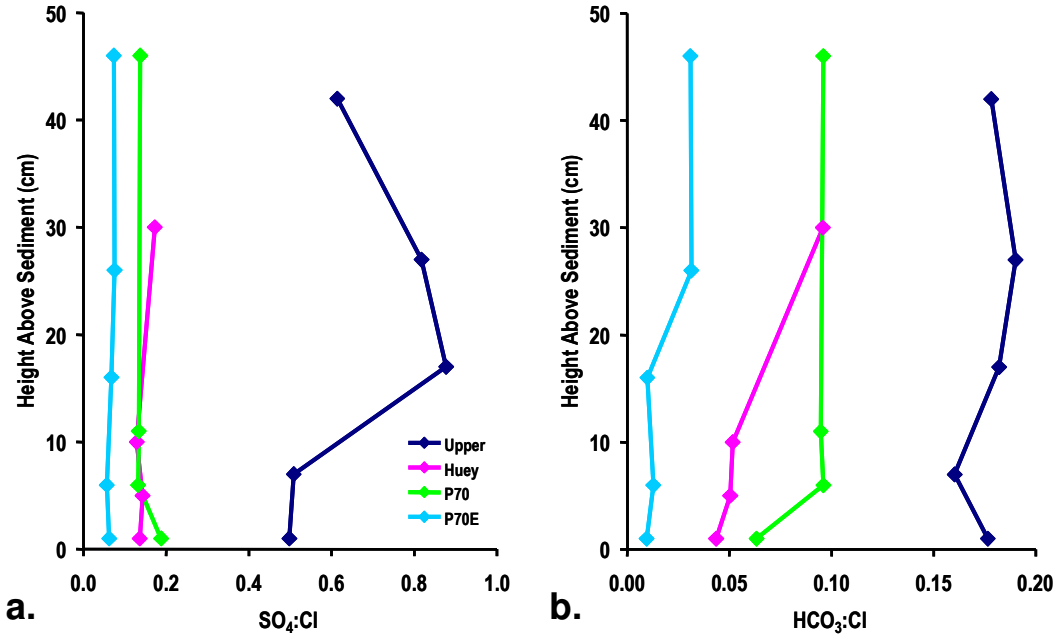

Figure 4.23 Graphs showing the ratio of major anions to Cl versus depth in four Bratina Island meltwater ponds in December 2005; a) SO_4 and b) HCO_3.

P70 Pond was chemically mixed through the water column and this is reflected in the ratio of cations and anions to Cl which showed no change with depth. VXE6 Pond showed a decrease in all ions, except Na, relative to Cl which may indicate the dissolution of a Na-Cl bearing mineral, such as halite (NaCl) or hydrohalite ($NaCl.H_2O$), at the base of the pond, effectively increasing the concentration of Na and Cl relative to all other ions. Orange Pond shows a significant increase in the ratio of HCO_3 to Cl at the top of the basal brine, while other ions behave reasonably conservatively at this depth. However, in the basal brine, Ca and HCO_3 decrease relative to Cl which may be indicative of precipitation of a Ca-CO_3 bearing mineral such as calcite.

Minerals identified in sediment samples from Bratina Island meltwater ponds included halite (NaCl), mirabilite ($Na_2SO_4.10H_2O$), thenardite (Na_2SO_4), magnesite ($MgCO_3$), gypsum ($CaSO_4$), sodium carbonate ($NaCO_3$) and calcite ($CaCO_3$). Therefore relative depletion of some ions in the

basal water column is likely related to mineral precipitation. A mineral such as dolomite ($CaMgCO_3$) or calcite ($CaCO_3$) could potentially remove Ca and HCO_3 ions simultaneously (e.g. P70 and Huey Ponds) while gypsum ($CaSO_4$) precipitation may explain a decrease in both Ca and SO_4 (e.g. Upper Pond) and relative Ca and HCO_3 depletion (e.g. Orange Pond) may indicate precipitation of a Ca-CO_3 bearing mineral such as calcite. Biological interaction may also influence non-conservative ion behaviour through photosynthesis and respiration processes, particularly in relation to SO_4 and HCO_3 as discussed in Section 4.5.7 and Chapter 6. In general, the ratios of major ions to Cl are conservative suggesting that changes in concentration of cations and anions are primarily the result of a concentration effect. These ratios also highlight the geochemical variability that occurs between meltwater ponds and within ponds over time.

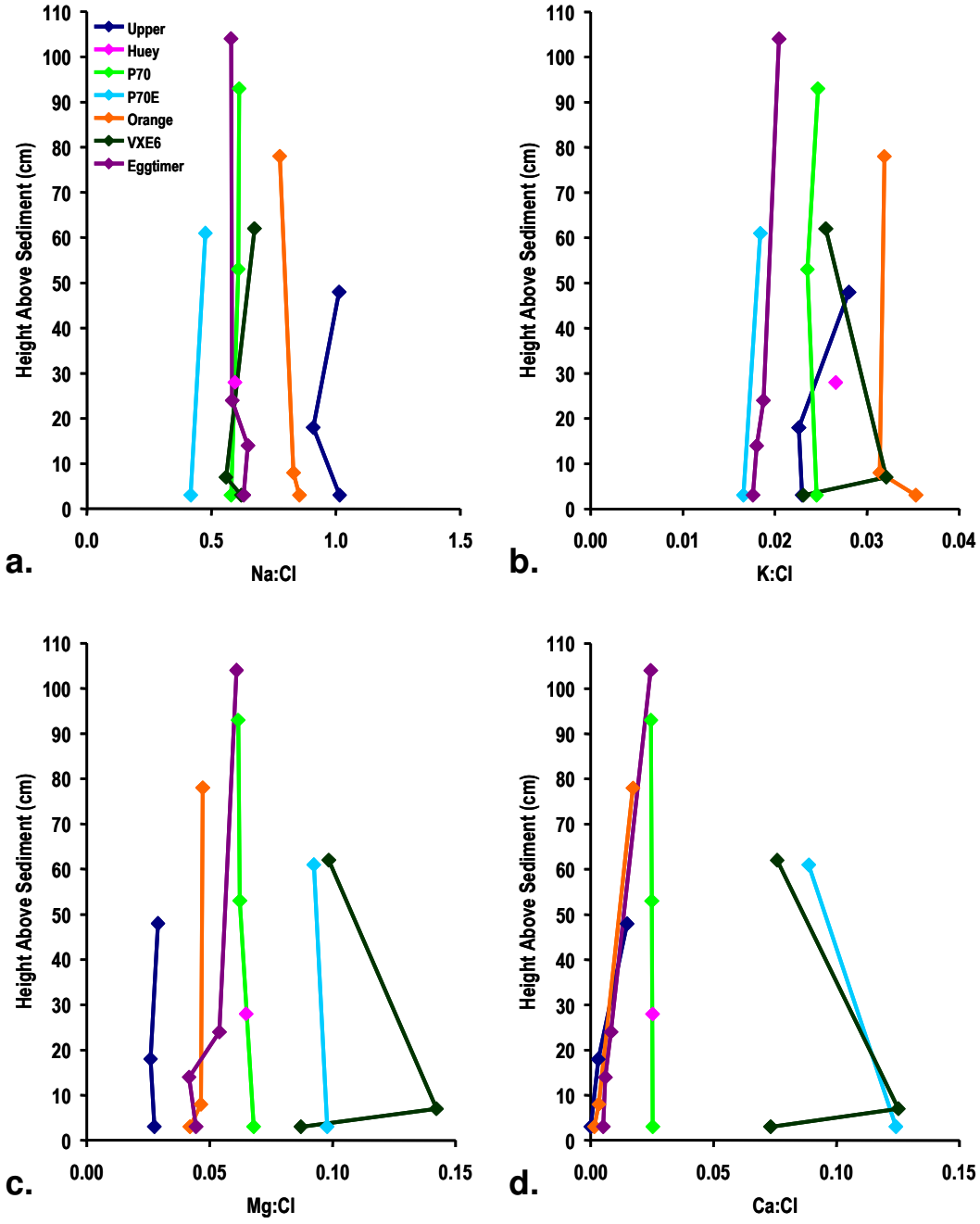

Figure 4.24 Graphs showing the ratio of major cations to Cl versus depth in seven Bratina Island meltwater ponds in January 2007; a) Na, b) K, c) Mg and d) Ca. Note that only a single sample was collected from the mixed water column of Huey Pond and is represented by a single point.

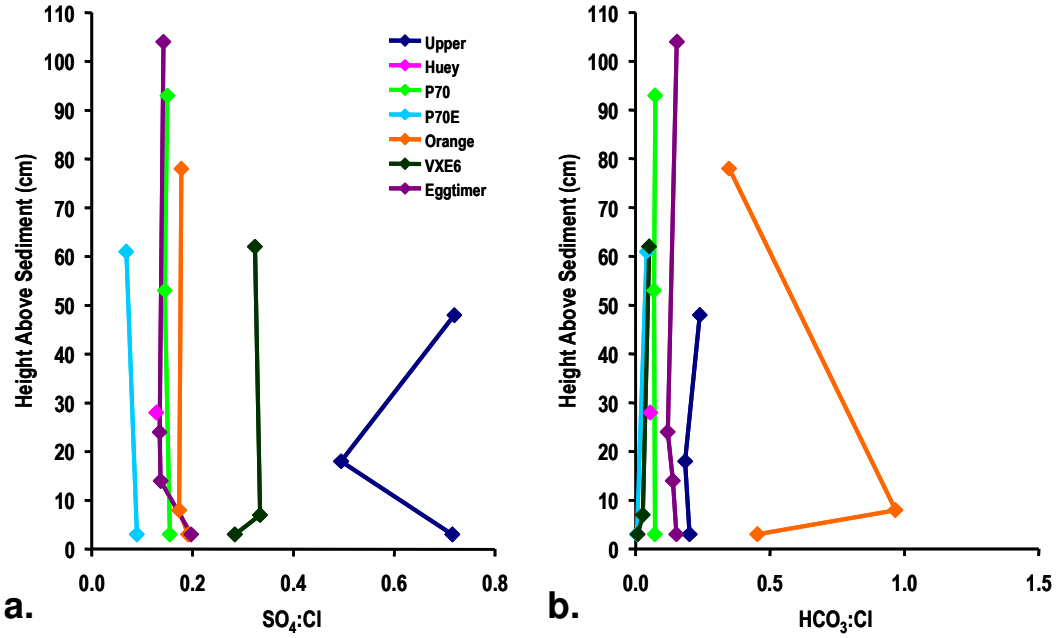

Figure 4.25 Graphs showing the ratio of major anions to Cl versus depth in seven Bratina Island meltwater ponds in January 2007; a) SO_4 and b) HCO_3. Note that only a single sample was collected from the mixed water column of Huey Pond and is represented by a single point.

4.5 Discussion 2: Factors Causing Geochemical Variation in Meltwater Ponds

4.5.1 The Freeze-Thaw Process

Vertical profiles in major ion concentrations and conductivity are primarily affected by the physical process of freeze-thaw, in particular the exclusion of salt from the downward progressing ice front during freezing and the presence of an ice plug during thaw. Both of these physical factors actively form and protect saline basal brines that persist into the summer period if catchment morphology (namely the relative depth of the pond, and the degree of shelter from the prevailing wind direction) allows.

Immediately post melting the four study ponds were significantly stratified, evidence of the ponds chemical stratification (ice and residual brine formation) during winter. The presence of basal brine during the early stages of melting indicated that salt exclusion had taken place during winter freezing. This is consistent with a downward progression of the freezing front and the exclusion of ions from newly formed ice to form a brine (Chapter 3), and with the observations made by Healy *et al.* 2006 and Wait *et al.* 2006 that frozen ponds preserve the stratification set up during the freezing process until spring / summer thaw. The presence of stratification immediately following the release of the ice plugs near the base of the ponds is also consistent with the presence of an ice plug preserving the basal brine into the summer period (Chapter 3).

In dynamic ponds repeatedly sampled during freezing in 2008, conductivity increases over time while temperatures and the concentration of DO decrease. Increasing conductivity over time reflects the exclusion of salt from newly formed surface ice as freezing progresses, resulting in increased major ion concentrations (and therefore conductivity) at the base of the ponds. Temperatures decrease over time as a result of reducing air temperatures and the loss of heat from the residual fluid beneath the ice to the atmosphere. Temperature spikes during the freezing period seen clearly in Orange Pond and Skua Pond in Figure 4.2 may be caused by the release of latent heat as discussed in detail in Chapter 3. Measurable concentrations of DO persisted beneath the thickening pond ice until in final measurements were taken in early April 2008, significantly longer than was expected. However concentrations did decrease steadily during this time. The persistence of DO in the residual fluid despite separation from the atmosphere by the ice cover indicates that biological processes may be continuing well into the winter period as long as light and liquid water is available. It may also be the result of DO exclusion into the brine from the growing ice (Killawee *et al.* 1998) which would prevent DO concentrations from becoming fully depleted.

Between the first collection of samples in early February 2008 to the last samples collected in late March or early April, the conductivity and concentration of major ions in the ponds increased as the thickness of the ice cover increased. This is a concentration effect as salt is excluded from the ice and concentrated into the residual water phase (see a description of this process in Section 4.1.2). However, concentration changes are not linear in all ponds. Figures 4.9 to 4.12, presented earlier in Section 4.3.4, show the major ion composition in just the basal water layer in dynamic meltwater ponds over time. Egg(timer) Pond and Orange Pond both show a decrease in the concentration of all major ions in the basal water layer (with the exception of Na in Orange Pond) in early March compared to early February samples indicating that the base of these ponds had become less saline. This suggests that convective mixing beneath the ice front had overcame some degree of the summer stratification and partially mixed the residual water phase, resulting in a relatively lower concentration of major ions at the base of the pond. The last sample taken from the base of these ponds (late March) shows an increase in major ion concentrations as would be expected given continued salt exclusion from the growing ice.

Therefore the freeze thaw process is a key factor causing geochemical variation in meltwater ponds; variation seen between different ponds on the MIS and within individual ponds at different times during the year.

4.5.2 Catchment Morphology

Long term (annual to decadal scale) seasonal variation is seen in the meltwater pond landscape on the MIS. Movement of the ice shelf causes cracks and collapse of the ice surface (Howard-Williams *et al.* 1990), erosion of the ice surface by running water leads to undercutting, pond merging and draining, and evaporation can significantly change the morphology of the ponds and ice shelf surface. Morphological changes to the pond catchment can change the chemical structure and composition of the meltwater ponds. In particular, the relative depth (RD) of a pond helps determine whether chemical stratification will be preserved during the summer melt period, catchment morphology determines exposure to prevailing winds and catchment size determines pond recharge.

The percent relative depth (RD) (Castro & Moore 2000) of a pond is an approximation defined by maximum water depth (Z_m) and average pond width (d) as shown in Equation 4.1.

$$RD = \frac{Z_m}{d} \times 100\% \qquad \textbf{Equation 4.1}$$

The percent relative depths calculated for meltwater ponds sampled in December 2005 and 2007 are shown in Table 4.10. Overall, the percent relative depth of the meltwater ponds is very high, ranging between 7.6 % and 22 %, compared to most natural water bodies which typically have a relative depth < 2 % although some may exceed 5% (Castro & Moore 2000). A high percent relative depth sets up the ideal conditions for stratification to occur although it does not guarantee its preservation (e.g. as in Eggtimer Pond and P70E Pond in 2007). Thus the morphology of a pond may predispose it to chemical stratification that can persist during the summer melt period. Of the four ponds sampled in 2005, two (Upper Pond and P70E Pond) remained stratified with a saline basal brine in the later 2007 sampling, largely reflecting the physical morphology of these ponds (i.e. relative depth) and their ability to resist mixing.

Table 4.10 Relative depth (RD) of meltwater ponds sampled in December 2005 and January 2007.

Pond	Year	Depth (m)	Diameter (m)	RD %	Year	Depth (m)	Diameter (m)	RD %
Huey	2005	0.5	2.95	16.9	2007	0.53	3.08	17.2
P70	2005	0.96	12.7	7.58	2007	1.10	14.5	7.59
P70E	2005	0.66	3.0	22.0	2007	0.81	3.78	21.4
Upper	2005	0.62	3.23	19.2	2007	0.67	3.49	19.2
VXE6					2007	0.92	4.85	19.0
Eggtimer					2007	1.55	7.5	21.0
Orange					2007	1.28	8.78	14.6

Pond catchment morphology determines a ponds exposure to the prevailing wind direction (south) which either encouraging mixing of the water column in exposed catchments or inhibiting mixing in sheltered catchments. Based on general observations made in the field, all ponds that were stratified in January 2007 were reasonably enclosed and sheltered from the wind suggesting that wind induced convection and mixing in the ponds was limited.

Catchment size and shape is a factor in determining the potential size of any water body within that catchment. The catchment size influences the amount of recharge available to each pond by determining its ability to collect and store snow which will subsequently melt and feed into the pond. Consequently, larger sized meltwater ponds were typically situated in the biggest catchments areas and visa versa.

4.5.3 Persistence of Stratification

The persistence of stratification, set up by the freeze-thaw process and the morphology of the pond catchment is a factor causing some of the geochemical variation seen in meltwater ponds. The chemical structure of meltwater ponds refers to the structure of the water column and whether a pond is fully mixed or stratified. The degree of temporal change in the chemical structure of each pond depends primarily on the density gradient with depth in the water column and the catchment morphology for each pond (i.e. relative depth in the pond; Section 4.5.2). The former determines the stability of the water column and the amount of energy required to overturn stratification, while the later affects the relative depth of the pond and the ponds exposure to prevailing winds, which determines the energy available for overturning stratification. It is the balance of energy required and energy available that will determine whether or not chemical stratification is retained throughout the summer period. In ponds retaining chemical stratification throughout summer, high conductivity basal brines were present at the base of the pond while mixed ponds were generally more dilute and water samples collected from different depths in the water column were similar in composition.

All ponds sampled in December 2005 immediately following melting were chemically stratified as discussed in the previous section, and some retained that stratification for the entire summer period up until refreeze. When sampled later in the summer season (January 2007) some ponds had retained chemical stratification while the water column in others had become fully mixed illustrating the spatial as well as temporal variation in meltwater ponds in the vicinity of Bratina Island. The conductivity of the basal brines was higher immediately post melting (39.3 – 74 mS cm^{-1}) compared to those measured at the end of January (35.1 – 36.1 mS cm^{-1}). This indicates that some mixing between the basal brine and the overlying water column occurred, either by

convection or diffusion, as summer progressed. Upper Pond showed only a slight decrease from 39.3 to 36.1 mS cm^{-1} in the basal brine indicating a high degree of water column stability, most likely due to the very high relative depth (19.2 %, see Table 4.10).

In late summer, as ponds began to refreeze (February 2008 sampling onwards), evidence suggests that some ponds had remained stratified for the entire summer period while others had not. Once refreeze commences (e.g. February 2008 samples onwards), the ability of a pond to retain stratification beneath the growing ice cover depends on the density gradient with depth and the degree of convective mixing, driven by salt exclusion, that takes place as freezing progresses. From the first 'dynamic' samples collected (early February 2008), Egg(timer) Pond, Orange Pond and Skua Pond (very slightly) showed some degree of stratification of major ions with depth beneath the growing ice cover, indicating that these ponds had maintained stratification for the entire summer. Conversely, P70 Pond appears mixed beneath the ice cover reflecting the fully mixed nature of the water column as freezing commenced; this is consistent with observations that P70 pond was fully mixed in January 2007.

4.5.4 Mineral Precipitation & Dissolution

The geochemical variation in the composition of meltwater is affected by the precipitation and dissolution of mineral phases. Mineral precipitation is mostly likely to occur in the high ionic strength basal brines that form during winter freezing but may be present at anytime during the year depending on the pond characteristics outlined above, while dissolution is more likely occur as concentrations of ions in solution become more dilute.

Figure 4.26 White salt deposits encrust sand and gravel around the edge of Brack Pond (January 2007). The green colouration and bubbles on the water surface are indicative of the high organic content of the pond.

During early thaw, several basal brines were slightly enriched in Na and SO_4 indicative of mirabilite dissolution as the pond melted out and became more dilute. Conversely, slight depletion of Ca and HCO_3 is perhaps indicative of a mineral phase (e.g. dolomite) that had precipitated out of the solution, remaining saturated despite dilution as the pond melted. This effective removal from the water column may occur if minerals are precipitated in the sediments or within cyanobacterial mat communities where chemical micro-environments may occur. Relative depletion of HCO_3 could also be linked to biological interaction with this ion through metabolic processes that occur at the interface between the cyanobacterial mat and the water column (Chapter 6).

A significant increase in bulk pond ion concentrations were observed in ponds that increased in depth during the summer period. This suggests that dissolution of salts from near edge sediments (Figure 4.26) and the hyporheic zone is an important source of major ions that may alter the composition make up of a pond.

4.5.5 Redox Conditions

Redox conditions may be a factor causing geochemical variation in meltwater ponds. Redox conditions can influence the solubility of minerals and determine whether certain ions will be bound up as precipitates or dissolved in solution contributing to the overall conductivity of the meltwater. In particular the presence or absence of dissolved oxygen will influence the speciation of the S ion as SO_4 or H_2S. Redox conditions in Bratina Island meltwater ponds will be discussed in Chapter 6.5.4.

4.5.6 Biological Processes

There is potential for biological processes to have an influence on the major ion chemistry of Bratina Island meltwater ponds, particularly in regard to concentrations of SO_4 and HCO_3 as interactions occur between the inorganic and organic forms of these ions (through the S and C cycles respectively). Biological processes can also affect the physical properties of meltwater ponds by altering the pH (with implications for HCO_3 concentrations) and DO concentration through the process of photosynthesis and respiration. For example, the disequilibrium observed between DO and Eh and DO and H_2S is likely to be the result of biological processes. The effects of biota on the geochemical properties of meltwater ponds will be discussed in detail in Chapter 6.

4.5.7 Timing of Field Sampling

The timing of summer sampling does not cause geochemical variation in meltwater ponds per se, but it can have a significant influence of the nature of the samples collected. This is due to temporal variation in the chemical composition of ponds that may result from any number of the following:

- Evaporation and precipitation and the subsequent change in pond depth and dilution or concentration of the pond chemistry;
- Changes in chemical structure of the pond, such as the loss of stratification and the formation of ice cover during freezing;
- Mineral precipitation, both temporary (e.g. from the development of basal brine) and permanent; and
- Degree of biological activity in the ponds at the time of sampling (for example this may be important when considering redox conditions and concentrations of major ions in the pond that may be influenced by biological processes).

4.6 Conclusions

The four distinct phases that occur in meltwater ponds during the annual cycle of freeze-thaw have a significant effect on the geochemical characteristics of ponds at different times during the year. The development of stratification during the freezing phase is well preserved until the end of the thaw phase when the isolating effect of the ice plug on the basal brine is visible through the rapid shift from anoxic to oxic conditions. Post ice plug melting, major ions show distinct vertical profiles consisting of an upper mixed layer and high density saline brine that remains at the base of the pond.

During the summer phase, meltwater pond geochemistry is dominated by NaCl with the chemical composition of ponds remaining similar between sampling years despite concentration changes. Basal brines were a significant feature of the summer melt period and remained fairly stable over the summer period. Conductivity in the basal brines was high (≤ 74 mS cm^{-1}) resulting in significant conductivity gradients between the surface and base of the ponds. The composition of the basal brine in Upper Pond, VXE6 Pond and Orange Pond deviated from the composition of the overlying water column evidence that processes other than concentration, such as mineral precipitation and dissolution, were influencing the brine. Catchment morphology and a ponds ability to preserve stratification were key factors influencing meltwater pond geochemistry. To a

lesser extent biological processes that are at maximum production along with redox, may have also been an influence.

The dynamic freezing phase is characterised by increasing major ion concentrations in the residual water phase as salt is excluded from thickening surface ice to form concentrated brine that may persist throughout winter. Interestingly, the composition of basal brines that developed during freezing was more similar to the basal brines persisting through the summer phase than the brines isolated beneath ice-plugs at the late stages of the thaw phase due to the depletion of ions from solution as minerals reach saturation and precipitate. Consequently, prediction of winter brine conditions should be based on mid-late summer pond compositions rather than those present immediately post thaw. Because summer stratification appears to be overturned by convection during freezing, brine evolution can be based on the bulk summer chemistry of both stratified and non stratified ponds with the assumption that just one series of ion fractionations occur in the residual fluid as freezing progresses. The ponds in this study were dominated by Na and Cl except Skua Pond which was dominated by Na and SO_4.

The factors that can cause geochemical variation in meltwater ponds include the freeze-thaw process, catchment morphology, persistence of stratification, mineral precipitation and dissolution, redox conditions and biological processes. These factors are inherently interlinked and do not occur as mutually exclusive system components meaning that the geochemical variation in a pond cannot be attributed to a single factor. However, the temperature driven freeze-thaw process and the formation of an ice plug is possibly the most significant factor influencing the meltwater pond geochemistry at the end of the thaw phase. In response to these factors, conditions may become thermodynamically favourable for mineral precipitation and dissolution. Most significant in the Bratina Island area is the dissolution and precipitation of mirabilite which enriches or depletes Na and SO_4 relative to Cl, as brines are formed and subsequently concentrate, dilute or mix, and as water levels fluctuate and saturate or expose new areas. Minerals identified in sediment samples from Bratina Island meltwater ponds included halite (NaCl), mirabilite ($Na_2SO_4.10H_2O$), thenardite (Na_2SO_4), magnesite ($MgCO_3$), gypsum ($CaSO_4$), sodium carbonate ($NaCO_3$) and calcite ($CaCO_3$) all of which have the potential to change the major ion composition of meltwaters.

Both spatial and temporal variation is evident within and between meltwater ponds. Spatial variation between ponds is not directly linked to conductivity and therefore the evaporative concentration of a single original meltwater; instead between-pond variation reflects the specific evolutionary history of each pond. Consequently, prediction of winter conditions must be based

on a thorough understanding of the summer chemistry of the specific pond of interest. Over time, some meltwater ponds show little change in the relative composition of cations and anion despite significant changes in concentration. Others show both compositional and concentration changes indicative of mineral dissolution as waters become more dilute over the summer period suggesting that repeat summer sampling is necessary for multi-seasonal research into winter brine conditions.

CHAPTER 5

SIMULATING MAJOR ION PROCESSES IN THE MELTWATER POND ENVIRONMENT

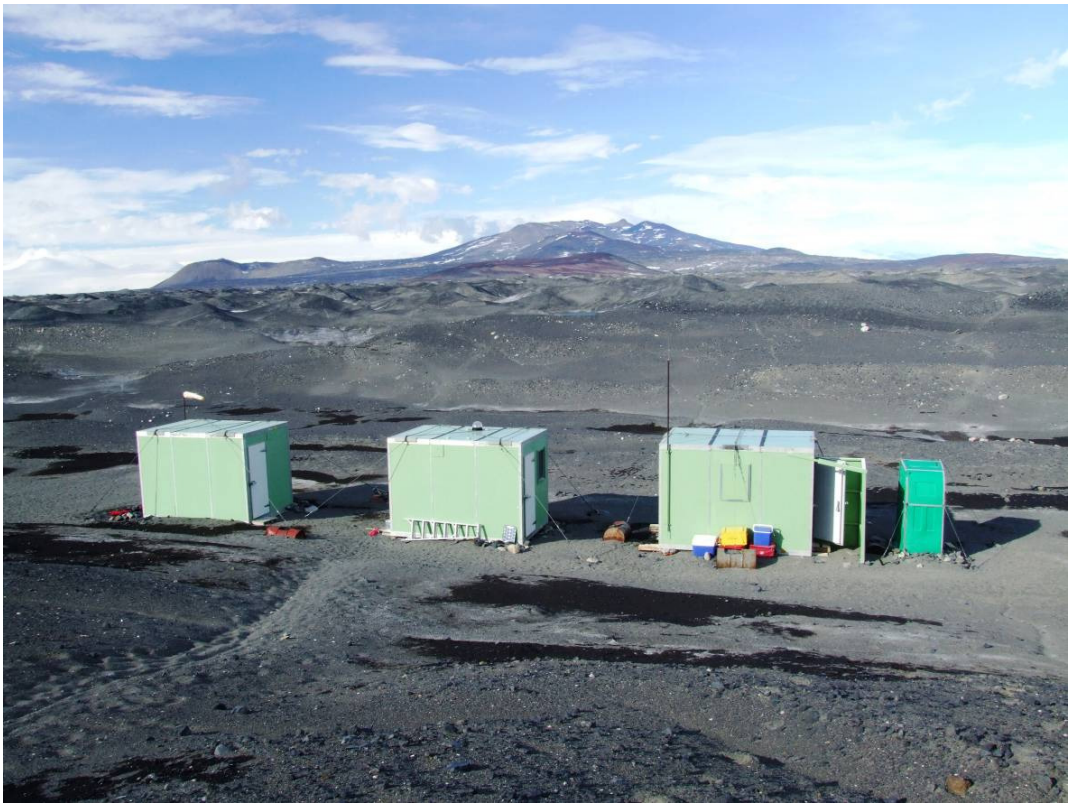

Figure 5. Bratina Island wanagan huts with view to Brown Peninsular in the distance, January 2007. From left to right: wet lab hut, dry lab hut, kitchen hut and toilet.

A significant limitation to understanding the meltwater pond environment is the lack of information pertaining to winter conditions in the ponds. Geochemical modelling is therefore an essential tool that can provide insight into the extreme chemistry of the winter environment. This chapter discusses the current understanding of the relationship between freezing and solution chemistry in relation to meltwater ponds. It presents the results from a series of water samples collected at different stages of freeze and thaw, and compares these results to solution chemistries derived using the geochemical model FREZCHEM.

5.1 Context of this Research

5.1.1 Chemical Pathways in the Freezing of Seawater

Variation in the initial chemistry of a meltwater pond has been shown to have a major influence on the composition of brines formed after evaporation and freezing (Green *et al.* 1988) making final brine compositions difficult to predict. Although meltwater ponds are inland water bodies, their widely varying salinity from fresh to hypersaline means that in some instances the solution chemistry is similar to that of seawater (for example the major ion composition of meltwater ponds presented in Chapter 4 of this study range from fresh to saline). For this reason the chemical pathways during the freezing of seawater are considered relevant to the meltwater pond environment (e.g. Thompson & Nelson 1956).

There is experimental evidence for two pathways for seawater freezing both beginning with the formation of ice at -1.9°C. The Ringer-Nelson-Thompson pathway involves the precipitation of mirabilite ($Na_2SO_4.10H_2O$) at -8.2°C, hydrohalite ($NaCl.2H_20$) at -22.9°C, sylvite (KCl) and a magnesium chloride salt ($MgCl_2.12H_20$) at -36°C, and finally antarcticite ($CaCl_2.6H_2O$) at -53.8°C, which is the eutectic temperature (the temperature at which the multi-component solution completely solidifies) for seawater freezing along this pathway (Marion *et al.* 1999; Marion & Kargel 2008). This pathway has been supported by other works; however, the experimental work of Gitterman in 1937 offered an alternative that includes the precipitation of gypsum ($CaSO_4.2H_2O$) (Marion *et al.* 1999; Marion & Kargel 2008). Along the Gitterman pathway the last salt to precipitate from the freezing of seawater is $MgCl_2.12H_20$ at the eutectic point of -36.2°C. The two pathways differ principally in the Ca salt that precipitates (antarcticite vs. gypsum) and the major difference in the eutectic temperature of seawater freezing (-53.8°C vs. -36.2°C).

Research by Marion (1997) suggests that the Gitterman pathway is more thermodynamically stable than the Ringer-Nelson-Thompson pathway and, more recently, this has been experimentally validated (Marion *et al.* 1999). Whereas other studies were based on short-term dynamic methods with equilibrium times measured in hours, Gitterman's research was based on static methods with equilibrium periods of up to four weeks. This allowed sufficient reaction times for mirabilite dissolution and gypsum precipitation. Also, freezing experiments at low temperatures involve a pre-concentration of seawater. The Gitterman method included the precipitated salts in the experiments as well as the solution phase, while others did not (Marion *et al.* 1999; Marion & Kargel 2008).

As a model, the Gitterman method allows the selection and configuration of both solid and solution phase constituents that minimise the Gibbs free energy of the system. This is particularly important as it was found that the SO_4 needed for gypsum precipitation comes from the dissolution of mirabilite alone (Marion *et al.* 1999; Marion & Kargel 2008). Therefore, if mirabilite is removed from a reaction site (i.e. through fractional crystallisation), it is not available for dissolution back into solution, and it would be impossible for gypsum to form.

The FREZCHEM62 model (described in Chapter 2.5.1) is an equilibrium chemical thermodynamic model that can be used to model progressive freezing and evaporation, chemical fractionation and equilibrium crystallisation. It can model high ionic strength (i.e. up to 20M) aqueous solutions across a range of temperatures (+25°C to -60°C), making it particularly suitable for modelling the meltwater pond environment. FREZCHEM62 is based on the Gitterman model of the chemical freezing pathway and includes solubility products for fifty solid phases, principally Cl, SO_4, NO_3 and HCO_3-CO_3 bearing minerals and including ice (Marion 1999).

5.1.2 Antarctic Applications of the Geochemical Model FREZCHEM

FREZCHEM (Marion *et al.* 1994) has been used as a tool for understanding cold temperature biogeochemical processes in many aqueous environments on Earth including seawater freezing, permafrost terrain, lakes and ponds (Marion *et al.* 1999; Marion *et al.* 2003b; Marion & Kargel 2008). It has also been used to investigate the surficial geochemistry of other planets such as Mars (Marion *et al.* 2003a; Marion & Kargel 2008) and Europa (Marion *et al.* 2003b; Marion *et al.* 2005, Marion & Kargel 2008) where cold aqueous processes play an important role. The FREZCHEM model can examine complex chemistries with up to eight independent components across a range of compositions with differing temperatures and pressures. This allows for a more realistic description of a natural system than simpler binary and ternary diagrams (Marion & Kargel 2008).

The FREZCHEM model has been used by several authors to look at cold temperature biogeochemistry in the Antarctic environment, focussing on lake water evolution in the MDV's lakes (Lyons *et al.* 2005), meltwater pond chemistry in Don Juan Pond (Marion 1997) and other ponds in the Wright and Victoria Valleys (Healy *et al.* 2006), and brine evolution and mineral precipitation in meltwater ponds on the MIS (Wait *et al.* 2006).

Don Juan Pond is unique in that it is the most saline Antarctic water body and is one of the few natural occurrences of the mineral antarcticite ($CaCl_2.6H_2O$) (Marion 1997). The FREZCHEM model was used to create theoretical mineral stability diagrams and to calculate the eutectic

temperature (-51.8°C) which explained the lack of freezing in the pond during winter despite the sub-zero air temperatures. The model predicted precipitation of the minerals halite and antarcticite which was compatible with data collected from the pond. This was the first time the FREZCHEM model was used in an Antarctic water body and demonstrated the model's usefulness in understanding physiochemical behaviour of saline water bodies at subzero temperatures.

The surface waters of Lake Fryxell and Lake Hoare in the MDV's were modelled using FREZCHEM to determine whether they could be cryo-concentrated to form brines similar to that found in the bottom waters of Lake Bonney (Lyons *et al.* 2005). Results indicated that the Na:Cl and SO_4:Cl ratios would be within range of those measured in Lake Bonney, however K:Cl would be enriched and Ca:Cl would be depleted in comparison; results from Lake Fryxell also indicated depletion in Mg:Cl. It was concluded that Lake Bonney bottom waters were not simply the result of freeze concentration of dilute Taylor Valley waters and that other processes were taking place (Lyons *et al.* 2005). During this modelling, minerals predicted to precipitate included hydrohalite ($NaCl.2H_2O$), sylvite (KCl), $MgCl_2.H_2O$, calcite ($CaCO_3$), mirabilite ($Na_2SO_4.10H_2O$), hydromagnesite ($3MgCO_3.Mg(OH)_2.3H_2O$) and nahcolite ($NaHCO_3$) (Lyons *et al.* 2005). Interestingly gypsum ($CaSO_4.2H_2O$) was not predicted to precipitate (Lyons *et al.* 2005) but this is arguably due to the requirement for mirabilite dissolution back into the brine to provide sufficient SO_4 for gypsum to occur (Marion *et al.* 1997).

The FREZCHEM52 model has previously been used to predict mineral precipitation during progressive freezing of meltwater ponds at Bratina Island (Wait *et al.* 2006). An initial bulk composition of each pond was calculated based on the composition and estimated volume of each stratified layer in the water column. Mirabilite and gypsum were predicted to occur during freeze concentration in all five ponds modelled (Skua, P70, P70E, Brack and Salt Ponds), as well as dolomite ($CaMgCO_3$) (P70E Pond) and a magnesium sulfate ($MgSO_4.12H_2O$) mineral (Brack and Salt Ponds) in some ponds. In comparison, only mirabilite, thenardite (Na_2SO_4 - dehydrated mirabilite), halite (NaCl) and carbonate were actually found in sediment samples from the area (Wait *et al.* 2006).

Similar modelling of mineral precipitation during progressive freezing was undertaken for meltwater ponds in Victoria Valley and the Labyrinth, Victoria Land, using FREZCHEM62 (Healy *et al.* 2006). Bulk chemistry was calculated that included the high NO_3 concentrations found in these inland ponds. Modelling predicted the following salts would precipitate; gypsum, mirabilite, magnesium sulfate, calcite ($CaCO_3$), dolomite and magnesite ($MgCO_3$). Salt collected from the

base of the ponds was always gypsum but hexahydrite ($MgSO_4.6H_2O$), blödite ($Na_2Mg(SO_4)_2.H_2O$) and iöweite ($Na_{12}(Mg_7(SO_4)_{13}.15H_2O$) was found alongside gypsum in the centre of a dry ephemeral pond, with thenardite, darapskite ($Na_3(NO_3)(SO_4).H_2O$) and nitratine ($NaNO_3$) and sometimes gypsum and halite around the edges (Healy *et al.* 2006).

In these previous studies, the FREZCHEM model had not been used to predict minerals that may form during evaporation of water bodies in Antarctica. This may explain the discrepancy between predicted and observed salts that most likely formed by evaporation, such as the presence of thenardite (Na_2SO_4) and halite (NaCl) as well as mirabilite ($Na_2SO_4.10H_2O$) and hydrohalite. The FREZCHEM62 model did not predict the formation of darapskite and nitratine in ponds in the Labyrinth (Victoria Land), but their presence in an ephemeral pond suggests these salts were precipitated as a result of subaerial evaporation or ice ablation of the pond, rather than during freeze concentration.

5.1.3 Contribution of this research

With limited access to meltwater ponds during extreme Antarctic winter conditions and a relative lack of field samples during this time, modelling becomes a critical if not the only way to understand what is happening in a meltwater pond during winter. Geochemical models (such as FREZCHEM) although available are not validated for the unique Antarctic environment.

Given that even a small amount of variation in the initial chemistry of a meltwater pond has been shown to have a major influence on the composition of brines formed after evaporation and freezing (Chapter 4; Green *et al.* 1988) and that many Antarctic ponds display a wide range of unusual water chemistries (e.g. Healy *et al.* 2006; Wait *et al.* 2006), it is very difficult to predict final brine chemistry based on freezing experiments in more temperate freshwaters or seawater environments (e.g. Thompson & Nelson, 1956). Therefore, the geochemical model FREZCHEM62 will be used to predict winter residual brine composition from initial bulk pond chemistry and these results will be compared to field data to validate this model. In addition, salts from cores at the base of meltwater ponds and from sediments in the catchment area will be collected and analysed, to validate the ability of FREZCHEM62 to predict mineral precipitation with accuracy. FREZCHEM62 will also be used to evaluate salt precipitation during meltwater pond evaporation, as well as during freezing, a process that has not been modelled in the past.

As in the previous chapter, meltwater ponds will be considered as both “static” water bodies indicating sampling at a single time point and as “dynamic” water bodies in cases where repeated samples were collected in a single season, allowing changes in the major ion composition of

meltwater ponds during progressive freezing process to be determined. It is hoped that this research will offer an improved understanding of the salt exclusion and brine evolution process in meltwater ponds, and will enable better prediction of the winter brine conditions likely to be found in ponds in this extreme environment when logistical constraints prevent field sampling.

5.2 Data Collection

Water samples were collected by the author at Bratina Island in December 2005 when the ponds first melted completely, in January 2007 when the ponds had been fully melted for some time. Water samples were also repeatedly collected by Ian Hawes and Karl Safi (NIWA) from Bratina Island ponds between February and April 2008 when the ponds were refreezing. Samples from 2005 and 2007 were stored and transported back to NZ where they were analysed for major ions (Na, K, Mg, Ca, Cl, SO_4, HCO_3) using HPIC, AAS and titration. A description of these analytical techniques is given in Chapter 2.3.1 and 2.3.3. Samples collected in 2008 were also analysed by Jenny Webster-Brown and Kevin Brown using these methods, and the data generously made available to this study.

In order to determine the types of minerals that were associated with meltwater ponds, a selection of sediment samples were collected from in and around Bratina Island ponds in December 2005 and January 2007, and analysed using SEM. Methods are described in Chapter 2.3.6. Two geochemical models were used, FREZCHEM62 and PHREEQC (Chapter 2.5) with the bulk composition of each pond being calculated using the methodology in Chapter 2.5.1.

5.3 Results

5.3.1 FREZCHEM62 Modelling Results of Static Ponds

Calculated bulk pond composition

Table 5.1 Calculated bulk pond chemistry of meltwater ponds included in this study for 2005 (if sampled) and 2007. Values represent g of ions per pond and the total volume of each pond is given in m^3.

Pond	Year	Na	K	Mg	Ca	Cl	SO_4	HCO_3	Volume
Upper Pond	2005	4010	92	111	44.0	3920	2720	709	1.7
	2007	2800	76	80	37.1	2780	1950	650	2.1
Huey Pond	2005	1480	55	186	45.5	2350	354	166	1.1
	2007	1200	54	130	50.7	2010	258	111	1.3
P70 Pond	2005	34900	1390	4550	1390	58300	8000	5570	40.3
	2007	62600	2490	6470	2560	103000	15300	7280	60.5
P70E Pond	2005	1700	61.6	381	300	3980	286	104	1.6
	2007	3400	132	669	657	7210	504	281	3.0
VXE6 Pond	2007	7670	299	1160	901	11400	3710	571	25.8
Orange Pond	2007	17000	698	1030	375	21900	3890	7640	5.7

A bulk pond composition is required for each meltwater ponds for input into the FREZCHEM62 model; this is achieved using the method described in Chapter 2.5.1. Results of these calculations, based on the results presented in Section 4.3.2 are shown for the 2005 and 2007 study ponds in Table 5.1 above:

FREZCHEM62 Modelling Results – Freezing Regime

The FREZCHEM62 results for progressive freezing of each meltwater pond under an equilibrium crystallisation regime are presented in Table 5.2. Dolomite ($CaMg(CO_3)_2$) was predicted to precipitate in all ponds with crystallisation occurring before freezing began in several ponds. Mirabilite ($Na_2SO_4.10H_20$) was also commonly predicted to occur between -3 and -7 ˚C, as was hydrohalite ($NaCl.2H_2O$) between -23 and -24 ˚C. The precipitation of gypsum ($CaSO_4.2H_2O$) and sodium bicarbonate ($NaHCO_3$) occurred in only one instance each (P70 Pond 2007 and Orange Pond 2007 respectively). In P70E Pond (2005), the model predicted the precipitation of sylvite (KCl) and $MgCl_2.12H_2O$, additionally this was the only pond where mirabilite was not predicted.

Table 5.2 FREZCHEM62 modelling results for static ponds in 2005 and 2007 near Bratina Island during a freezing regime between 5˚C and the temperature at which the eutectic point was reached. Temperatures (˚C) indicate the first appearance of the mineral; when a temperature range is given the mineral was present only at those temperatures.

Pond	Year	$CaMg(CO_3)_2$	$MgCO_3$	$Na_2SO_4.10H_2O$	$CaCO_3$	$NaCl.2H_2O$	$CaSO_4.2H_2O$	$NaHCO_3$	KCl	$MgCl_2.12.H_2O$
Upper	2005	5	5	-3						
	2007	5	5	-3		-22				
Huey	2005									
	2007	-1		-7	-20	-23				
P70	2005	5		-7		-23				
	2007	5		-6	-22 – -23	-23	-24			
P70E	2005	5 - 2; -1; -6 - -9				-24			-38	-37
	2007	5 – 2;			3	-24	-5		-29	-28
Orange	2007	5	5	-5		-22		-23		
VXE6	2007	5	-25	-6		-25	-2			

FREZCHEM62 modelling ceased at the eutectic point (defined by the model as being reached when 7 mineral phases were precipitating simultaneously) in each pond. Table 5.3 shows the temperature at which this point was reached in each static meltwater pond and the mineral phases that occurred at that point.

Table 5.3 Minerals precipitating at the eutectic temperature (˚C) for each of the static meltwater ponds modelled using FREZCHEM62 for a freezing regime.

Pond	Year	Temp.	Minerals precipitating at eutectic									
			H_2O	$NaCl.2H_2O$	KCl	$MgCl_2.12.H_2O$	$Na_2SO_4.10H_2O$	$CaSO_4.2H_2O$	$CaCO_3$	$MgCO_3$	$NaHCO_3$	$CaMg(CO_3)_2$
Upper	05	-24	x	x	x		x			x	x	x
	07	-24	x	x	x		x			x	x	x
Huey	05											
	07	-24	x	x			x	x	x			x
P70	05	-25	x	x			x	x		x		x
	07	-25	x	x			x	x		x		x
P70E	05	-41	x	x	x	x		x	x			
	07	-30	x	x	x	x		x	x			
Orange	07	-24	x	x	x		x			x	x	x
VXE6	07	-25	x	x			x	x		x		x

FREZCHEM62 Modelling Results – Evaporation Regime

The FREZCHEM62 results for progressive evaporation of each meltwater pond under an equilibrium crystallisation regime are presented in Table 5.4. Dolomite ($CaMg(CO_3)_2$) was predicted to precipitate in all ponds with crystallisation occurring before evaporation began, indicating saturated conditions, in all but Huey Pond (2007). Magnesite ($MgCO_3$) was also at saturation prior to evaporation in Upper Pond (2005) and Orange Pond and was predicted to occur at varying degrees of evaporation in all but P70E Pond. Mirabilite ($Na_2SO_4.10H_20$), hydrohalite ($NaCl.2H_2O$) and gypsum ($CaSO_4.2H_2O$) occurred in a selection of pond as the remaining water decreased to 60 g or less, with hydrohalite only occurring in the final 10 g of water.

Table 5.4 FREZCHEM62 modelling results for static ponds in 2005 and 2007 near Bratina Island during an evaporation regime at 5˚C, with initial water of 1000 g reducing to 10 g in 10 g increments. Water weights indicate the first appearance of each mineral; once present all minerals remained until the final water weight (except dolomite in VXE6 Pond).

Pond	Year	$CaMg(CO_3)_2$	$MgCO_3$	$CaSO_4.2H_2O$	$NaCl.2H_2O$	$Na_2SO_4.10H_2O$
Upper	2005	1000	1000		7.3	60
	2007	1000	890			30
Huey	2005	1000	140	20		
	2007	910	10	10		
P70	2005	1000	40	10		
	2007	1000	10	20		
P70E	2005	1000		60	10	
	2007	1000		60	10	
Orange	2007	1000	1000		9.1	40
VXE6	2007	1000-30	20	130	10	

5.3.2 FREZCHEM62 Modelling Results of Dynamic Ponds

Calculated bulk pond composition

The bulk pond composition (presented in Table 5.5) was calculated for the four dynamic ponds based on the composition of January/early February 2008 water samples collected prior to pond freezing. Composition totals reflect the total pond volume.

Table 5.5 Bulk pond chemical composition for four meltwater ponds sampled in 2008. Values represent g of ions per pond and the total volume of each pond is given in m^3.

Pond	Na	K	Mg	Ca	Cl	SO_4	HCO_3	Volume
P70 Pond	50100	1540	3780	2660	39400	63500	29500	37
Orange Pond	11000	537	712	118	15400	2280	2540	14.4
Egg(timer) Pond	38900	1780	3620	1710	65100	10000	2540	31
Skua Pond	30700	1240	5760	664	55600	5470	10100	204

FREZCHEM62 Modelling Results – Freezing Regime

Table 5.6 FREZCHEM62 modelling results for dynamic meltwater ponds in 2008 near Bratina Island during a freezing regime between 5˚C and the temperature at which the eutectic point was reached. Temperatures (˚C) indicate the first appearance of the mineral; when a temperature range is given the mineral was present only at those temperatures.

Pond	$Na_2SO_4.10H_2O$	$MgCO_3$	$CaMg(CO_3)_2$	$NaCl.2H_2O$	$CaCO_3$	KCl	$NaHCO_3$
P70	-6		-1	-23	-15		
Orange	-6	-1	5 - 3; -1	-22		25	
Egg(timer)	-9	5	5	-23			
Skua	-2	-1	-1	-23			-21

Based on the chemistry of each pond prior to freezing, each dynamic meltwater pond predicted the precipitation of mirabilite, dolomite and hydrohalite; calcite and sylvite were also predicted to occur in individual ponds (P70 and Egg(timer) Ponds respectively). The results of this modelling are shown in Table 5.6 and the temperature at which the eutectic point was reached (and corresponding minerals) are shown in Table 5.7 below.

Table 5.7 Minerals precipitating at the eutectic temperature (˚C) for each of the static meltwater ponds (2008) modelled using FREZCHEM62 for a freezing regime.

		Minerals precipitating at eutectic									
Pond	Temp.	H_2O	$NaCl.2H_2O$	KCl	$MgCl_2.12.H_2O$	$Na_2SO_4.10H_2O$	$CaSO_4.2H_2O$	$CaCO_3$	$MgCO_3$	$NaHCO_3$	$CaMg(CO_3)_2$
P70	-24	x	x			x	x	x			x
Orange	-26	x	x	x		x	x		x		x
Egg(timer)	-25	x	x			x	x		x		x
Skua	-24	x	x	x		x			x	x	x

A comparison is made in Table 5.8 between the initial bulk pond composition of dynamic meltwater ponds (i.e. bulk pond composition based on fully melted ponds in late January and

early February 2008), the bulk pond composition after a period of freezing (i.e. bulk pond composition based on the final sample collected in late March or early April 2008) and FREZCHEM62 modelled composition at the corresponding stage of melt (based on the % ice volume of each pond). The two minerals predicted to precipitate by FREZCHEM62 were magnesite and dolomite.

Table 5.8 Initial (based on late January and early February 2008 samples), final (based on late March and early April 2008 samples) and modelled bulk pond composition of dynamic meltwater ponds at the equivalent ice volume (%).

Pond	Time	Ice %	Total Major Ion Composition (g/pond)						
			Na	K	Mg	Ca	Cl	SO_4	HCO_3
Skua	initial	0%	50100	1540	3780	2660	39400	63500	29500
	final	76%	43500	1410	2770	1990	33800	53400	16100
	modelled	76%	50100	1540	347	50	30500	63500	3960
Orange	initial	0%	11000	537	712	118	15400	2280	2540
	final	86%	9170	386	548	6	13500	1830	3490
	modelled	86%	11000	537	338	34	15400	2280	390
P70	initial	0%	39000	1780	3620	1710	65100	10000	2540
	final	40%	40200	1630	3860	1170	70500	10100	2490
	modelled	40%	39000	1780	3550	1600	66400	10000	1860
Egg(timer)	initial	0%	30700	1240	5760	664	55600	5470	10100
	final	86%	18000	646	2360	216	30200	3310	3560
	modelled	86%	30700	1240	4600	469	55600	5470	3610

5.4 Discussion: FREZCHEM62 Modelling Results

The apparent mixing of summer basal brines into the water phase beneath growing ice is significant in our understanding of brine evolution during winter freezing as it indicates that under ice convection is sufficient to overturn summer stratification. If summer basal brines were preserved at the base of stratified ponds throughout the entire freezing process then winter basal brine compositions could not be easily predicted as further fractionation would occur each year. In other words, the basal brine present during summer would evolve during winter to then be preserved (with the help of an ice plug) in some form during the following summer, only to be fractionated a subsequent time the following winter. In order to model this process, the composition of the basal brine in each pond would need to be determined in summer each year and modelled for the winter immediately following, which given the logistical constraints associated with Antarctic research is not a viable option. However, because summer stratification appears to be overturned by convection during freezing, brine evolution can be based on the bulk summer chemistry of the pond with the assumption that just one series of ion fractionations occur in the residual fluid as freezing progresses. Essentially, this means that both stratified and non stratified ponds can be treated the same when predicting winter brine compositions.

5.4.1 Modelling of Freezing & Evaporation using FREZCHEM62

Mineral Precipitation during Progressive Freezing

In general, the minerals predicted to precipitate in meltwater ponds near Bratina Island, were consistent with what has been observed in the area. Of the 9 minerals predicted to precipitate (specifically $Na_2SO_4.10H_2O$, $MgCO_3$, $CaMg(CO_3)_2$, $NaCl.2H_2O$, $CaCO_3$, $CaSO_4.2H_2O$, $NaHCO_3$, KCl and $MgCl_2.12.H_2O$) at least 5 (possibly 7) were observed in sediment and salt samples from the area. However differences occur between predicted results and observed results in some instances (see Table 5.9). This may be in part due to assumptions made when calculating the initial bulk chemistry for each pond, such as a cone shaped basin based on depth and a mean diameter, which determines the volume of water in each layer and the relative contribution of brine layers to the overall chemical composition. It may also reflect processes that are occurring within the pond environment during freezing that are not accounted for by the FREZCHEM62 model as will be discussed in Section 5.4.3.

Table 5.9 Minerals predicted to precipitate by the FREZCHEM62 model under a freezing regime (unshaded areas); shaded areas indicate that minerals were not predicted by the model. In P70E and Upper Pond the minerals actually observed in sediment samples are indicated by the letter O.

Mineral	Upper		Huey		P70		P70E		Orange
	2005	2007	2005	2007	2005	2007	2005	2007	2007
$Na_2SO_4.10H_2O$	O	O							
$MgCO_3$									
$CaMg(CO_3)_2$	O?	O?							
$NaCl.2H_2O$							O	O	
$CaCO_3$	O	O					O	O	
$CaSO_4.2H_2O$							O	O	
$NaHCO_3$									
KCl									
$MgCl_2.12H_2O$									

Observations of certain minerals in the ponds that were not predicted by FREZCHEM62 may reflect the fact that these minerals had been removed permanently from the solution leaving the ions necessary for precipitation lacking. For example, the relative lack of SO_4 and HCO_3 in P70E Pond compared to Cl explains the predicted absence of some SO_4 and CO_3 minerals, however, the observed presence of gypsum and calcite in the pond likely explains how these concentrations came to be so low. In the case of sylvite (KCl) which is predicted to form at or near the eutectic temperature in most of the study ponds, sediment/salt samples would need to be collected from the base of the pond in mid winter to coincide with temperatures conducive to sylvite precipitation.

Although each pond was predicted to precipitate a slightly different mineral assemblage, the first appearance of each mineral occurred at similar temperatures (see Table 5.10). For example, dolomite ($CaMg(CO_3)_2$) often begun precipitating immediately (at 5˚C) or near 0˚C. Similarly, mirabilite was predicted to occur between -3 ˚C and -7 ˚C. This suggests that despite differences in the initial pond chemistry, precipitation pathways are similar in all ponds. Where the predicted mineral assemblage in a pond differs from others, such as the case in P70E Pond which was the only pond in which mirabilite was not predicted to occur, this reflects the relative abundance of ions in the original solution. In P70E Pond, concentrations of SO_4 were relatively low compared to other ponds; therefore SO_4 bearing minerals such as mirabilite were not predicted to reach saturation.

Table 5.10 Minimum and maximum temperatures (˚C) at which minerals predicted to precipitate in static meltwater ponds by the geochemical model FREZCHEM62 first occurred.

Mineral	T_{MIN}	T_{MAX}
$Na_2SO_4.10H_2O$	-7	-3
$MgCO_3$	5	5
$CaMg(CO_3)_2$	-1	5
$NaCl.2H_2O$	-24	-22
$CaCO_3$	-20	-20
$CaSO_4.2H_2O$	-24	-24
$NaHCO_3$	-23	-23
KCl	-38	-38
$MgCl_2.12H_2O$	-37	-37

Mineral Precipitation during Progressive Evaporation

Evaporation pathways, as determined by FREZCHEM62, vary slightly between ponds depending on their major ion composition. As indicated by the freezing regime modelling, dolomite was predicted to occur in all ponds during evaporation and was present at saturated levels (according to the model) prior to evaporative concentration in several cases. Six minerals were found precipitated in the sediments surrounding meltwater ponds on the MIS; these salts were either in the soil or formed a scale-like crust on gravel sized sediments. These observed minerals are compared to the minerals predicted by FREZCHEM62 to precipitate during evaporation in Table 5.11. Only sodium bicarbonate was found in the field but not predicted to occur in any pond following evaporation, suggesting that FREZCHEM62 predictions are generally valid. Mirabilite and hydrohalite were predicted to occur during evaporation, rather than thenardite or halite as residual water remained at the end of each modelling run, however, complete evaporation of meltwater ponds is likely to result in precipitation of the anhydrous version of these salts.

In an evaporated pond in the Labyrinth, at the head of the Wright Valley, Victoria Land, the mineral assemblage observed included gypsum, hexahydrite ($MgSO_4.6H_2O$), blödite ($Na_2Mg(SO_4)_2.H_2O$), iöweite ($Na_{12}(Mg_7(SO_4)_{13}.15H_2O$), thenardite, darapskite ($Na_3(NO_3)(SO_4).H_2O$), nitratine ($NaNO_3$) and occasional halite (NaCl) (Healy *et al.* 2006). Of these minerals only gypsum, halite (as hydrohalite) and thenardite (as mirabilite) were predicted to occur or actually found in or around MIS ponds. The lack of NO_3 minerals is due to the very low concentrations of NO_3 measured in MIS ponds (Hawes *et al.* 1993; Hawes *et al.* 1999) and the unlikelihood that NO_3-bearing minerals would reach saturation. Calcium sulfate minerals (e.g. gypsum) are more common than the Mg-SO_4 minerals observed inland.

Table 5.11 Minerals predicted to precipitate by the FREZCHEM62 model under an evaporative regime (unshaded areas); shaded areas indicate that minerals were not predicted by the model. In P70E and Upper Pond the minerals actually observed in sediment samples are indicated by the letter O.

Predicted Mineral	Upper		Huey		P70		P70E		Orange
	2005	2007	2005	2007	2005	2007	2005	2007	2007
$Na_2SO_4.10H_2O$		O							
$MgCO_3$									
$CaMg(CO_3)_2$		O							
$NaCl.2H_2O$							O		
$CaSO_4.2H_2O$							O		
$NaCO_3$									
$CaCO_3$		O					O		

5.4.2 Effectiveness of FREZCHEM62 at modelling meltwater pond freezing

By using FREZCHEM62 to model the development of brine during freezing in those ponds sampled repeatedly during the freezing phase in 2008, the effectiveness of FREZCHEM62 in replicating this process can be assessed. Different steps in the freezing process in each of the ponds were matched to the corresponding modelled stage using the thickness of the ice cover at the time of sampling to the percentage of ice predicted to have precipitated using the FREZCHEM62 model. This enabled the FREZCHEM62 modelled brine composition to be compared to the actual composition of brine sampled; results are presented side by side in Table 5.12 along with the ratio of modelled bulk pond composition to field bulk pond composition.

Ratios indicate significant depletion in Mg and Ca and HCO_3 in Skua Pond in predicted results compared to those observed, and although this is consistent with predictions that both magnesite and dolomite would precipitate, over prediction is likely. Additionally, water samples indicate that Skua Pond is mixed in summer but little visibility through the water column prevents pockets of brine, if present, from being identified. This could also explain higher concentrations in observed

brine compositions compared to those modelled if small amounts of basal brine were not included in bulk pond calculations.

Low modelled concentrations of HCO_3 present in Orange Pond may also indicate over prediction of carbonate minerals. Although modelled Ca in Orange Pond was significantly higher (~6 times) than the field results, given the very low quantities of Ca for the pond, the actual difference was very minor (28 g/pond). In P70 Pond, the FREZCHEM62 predicted pond composition was not significantly different from the field based composition and modelled results gave a good approximation of the field composition. Interestingly, this was the only pond where the bulk composition was based on a fully mixed water column. In Eggtimer Pond the composition based on field measurements are nearly half those predicted by FREZCHEM, except for HCO_3 for which the ratio is essentially 1:1. This may indicate that significantly more mineral precipitation is occurring in the field than is predicted by FREZCHEM62 or that the bulk pond chemistry calculated for this pond was significantly over estimated. Given the potential for errors during the calculation of bulk pond compositions, such as in the estimation of total pond volume and layer volume, overall FREZCHEM62 gave a reasonable approximation of the brine formation process. Where results were inconsistent this suggests that processes not accounted for by FREZCHEM62 could be operating such as incomplete salt exclusion from the ice that was evidenced in Chapter 3. The potential limitations of using FREZCHEM62 for the meltwater pond environment are discussed in Section 5.4.3.

Table 5.12 FREZCHEM62 predicted brine composition compared to actual brine composition (based on final 2008 field sampling) during progressive freezing in dynamic meltwater ponds sampled in 2008. The ratio of modelled bulk pond composition to field bulk pond composition is also shown.

Pond	Time	Ice %	Total Major Ion Composition (g/pond)						
			Na	K	Mg	Ca	Cl	SO_4	HCO_3
Skua	final	76%	43500	1410	2770	2000	33800	53400	16100
	modelled	76%	50100	1540	347	50	30500	63500	3960
	ratio		1.15	1.09	0.13	0.03	0.90	1.19	0.25
Orange	final	86%	9170	386	548	6	13500	1830	3490
	modelled	86%	11000	537	338	34	16600	2280	390
	ratio		1.20	1.39	0.62	6.03	1.23	1.24	0.11
P70	final	40%	40200	1630	3860	1170	70500	10100	2490
	modelled	40%	38900	1780	3550	1600	66400	10000	1860
	ratio		0.97	1.09	0.92	1.37	0.94	0.99	0.75
Egg(timer)	final	86%	18000	646	2360	216	30200	3310	3560
	modelled	86%	30700	1240	4600	469	56600	5470	3610
	ratio		1.71	1.93	1.95	2.17	1.87	1.65	1.01

5.4.3 Potential limitations of applying FREZCHEM62 to meltwater ponds

Parameterization & Mathematical Modelling

One of the main limitations of the FREZCHEM62 model, as with any other geochemical model, is the comprehensiveness and accuracy of the chemical database. For example, parameters and equilibrium relationships at sub-zero temperatures are less readily available and may require extrapolation from the above-zero data available (Marion & Kargel 2008). While these pitzer-equation parameterization limitations exist for the FREZCHEM62 model, the components that make up the meltwater pond composition are relatively well understood and this is unlikely to be a major cause of inaccuracy in this case.

The mathematics behind the FREZCHEM62 model requires the initial conditions to be balanced and for linked parameters (such as pH and acidity [H^+]) to be sufficiently close for convergence to occur (Marion & Kargel 2008). Additionally, the mathematics of the model requires an aqueous phase to be present at all times. If a point at which the ice and mineral phases are unable to simultaneously reach equilibrium (such as at or beyond the eutectic) then the model will cycle repeatedly through the ice and salt phases failing to reach thermodynamic equilibrium (Marion & Kargel 2008). This poses a potential problem when modelling meltwater ponds as complete freezing of the aqueous phase may occur during winter; with residual basal brine being observed in only 3/5 ponds in October 2001 (Wait *et al.* 2006).

Environmental Disequilibrium

The natural disequilibrium that occurs in any environment poses perhaps the greatest limitation of the FREZCHEM62 model. In meltwater ponds, there are key physical, chemical and biological processes that occur that cannot be accounted for when using the FREZCHEM62 model. Firstly, the model assumes complete exclusion of major ions from ice during freezing. This is problematic as several studies have shown salt incorporation within the crystal structure of the ice and in interstitial cavities during freezing (e.g. Cragin 1995; Fairchild *et al.* 1996; Medjani *et al.* 1996; Killawee *et al.* 1998; Iliescu *et al.* 2002) as described below.

Pure water solidifies at a constant temperature with two distinct phases, a liquid and a solid (Medjani *et al.* 1996). Conversely, a brackish or saline water body is a multi-component system with the concentration of solute in the system determines the temperature at which the phase change will occur. This results in three phases, a solid, a liquid and a "mushy" solid-liquid phase where residual fluid is trapped within a dendritic structure of crystals (Medjani *et al.* 1996). It is this mushy phase that may lead to the formation of brine pockets if trapped within the downward

growing freezing front. This trapping is thought to occur as a result of "necking" of the brine channel, with the channel walls freezing inwards (Medjani *et al.* 1996). The incorporation of brine into the forming ice as brine channel and pockets prevents the formation of a single evolving brine pool from which mineral saturation can be calculated. Additionally, convection of the liquid trapped within brine channels may lead to secondary brine evolution (as discussed in Chapter 3.4.6) and if the ionic strength of the brine increases, channels may coalesce and pockets of brine may form.

In a study of the exclusion of NaCl from ice during freezing found that at concentrations < 3000 mg L^{-1} NaCl, salt can be incorporated within the ice lattice as well as at the grain boundaries however at higher concentration brine pockets were formed (Cragin 1995). In another study of the microstructural and microchemical features of pond ice in a fresh water environment, impurities have been found to concentrate along grain and subgrain boundaries (Iliescu *et al.* 2002) without the formation of brine pockets.

Solute rich aqueous inclusions may lead to further reactions during cooling after ice formation (Killawee *et al.* 1998). Ferrick (1998) found a single lake ice sample enriched compared to other ice samples and hypothesised that the enriched water was from midwinter ice melt that pooled and then reincorporated into the ice when growth resumed, fractionating a 2nd time. Laboratory testing on non-stratified, quiescent water supported this hypothesis indicating that melt layers formed, persisted and were reincorporated into the ice during refreeze with a second fractionation and exclusion (Ferrick *et al.* 2002). Similar enriched layers were observed by Wait *et al.* 2006 in P70E Pond and attributed to brine pockets.

The existence of brine channels in meltwater pond ice was reported by Wait *et al.* (2006) where thick and thin sections of an ice core revealed vertical brine channels in Skua Pond increasing with frequency with increasing depth. At the base of the ice core the ice became structurally more complex, the ice became horizontally discontinuous, and the brine channels coalesced from fine individual channels into clustered, thicker features (Wait *et al.* 2006). The presence of brine channels were thought to explain the apparent increase in the chemical concentration of ice partway through the water column in some meltwater ponds (Wait *et al.* 2006). Additionally, differences in the rate of vertical heat transfer during warming and cooling periods in Skua Pond (see Chapter 3.4.3) support the presence of brine channels and the likelihood of secondary chemical fractionation.

In another study that focused on the precipitation of calcite during progressive freezing, geochemical modelling predicted an increase in PCO_2 and the saturation state of calcite as ice

growth occurred (Fairchild *et al.* 1996). It was found that during the freezing of CO_2-saturated solutions, $CaCO_3$ precipitation cannot be considered an equilibrium process, with morphological (and chemical) heterogeneity illustrating the importance of micro-environments within the evolving chemical system (Fairchild *et al.* 1996).

A second cause of natural disequilibrium is reaction kinetics. FREZCHEM62 predicts the precipitation of minerals on a thermodynamic basis, but kinetic effects, driven by biotic or abiotic factors, may also influence minerals precipitation. Reaction kinetics may be fast or slow in a system, with both reactants and products present in the system at the same time. This differs significantly from FREZCHEM62 which assumes that the minimum energy state is achieved at all times and that reactions are complete and instantaneous (Marion & Kargel 2008). Although H_2S is not a major component of meltwater pond composition it can have a significant effect on the precipitation of certain minerals, particularly trace metals, as discussed in Chapter 3.4.6. The incongruous presence of H_2S in fully oxidised meltwater pond systems is just one indication that reaction kinetics may be slow or that kinetic barriers are in place that prevent thermodynamic equilibrium being reached. Slower reaction kinetics may be significant cause of discrepancies between FREZCHEM62 predictions and observed conditions.

Finally, the disequilibrium in natural systems caused by biological processes can limit the potential of FREZCHEM62 to accurately predict chemical conditions as the influence of biological communities on the chemistry of the environment and the precipitation of minerals, cannot be accounted for. The potential for biological systems to drive chemical reactions and create micro-environments that differ from the surrounding environment is great. Metabolic activity can act as both a catalyst and an accelerant in chemical reactions, as well as producing stable intermediate species that would not otherwise exist (Marion & Kargel 2008). Any interaction between metabolic schemes and ionic species or complexes can have a major effect on evaporitic and freezing chemistry such as that dealt with by FREZCHEM62 (Marion & Kargel 2008). For example, sulfur geochemistry is closely linked with the microbially driven biogeochemistry of sulfur, with microbial activity providing a key source of soluble sulfate as well as mediating sulfur cycling (Marion & Kargel 2008). For example, the precipitation of dolomite does not readily occur in the presence of sulfate without microbial mediation such as that of sulfate reducing bacteria (Van Lith *et al.* 2003). In Bratina Island meltwater ponds, benthic cyanobacterial mats and the underlying anaerobic micro-environments are a known site for bacterially mediated methanogenesis and sulfate reduction (Mountfort *et al.* 1999; Mountfort, *et al.* 2003) as well as acting as a potential source of biogenic sulfur compounds (de Mora *et al.* 1996). This indicates

that metabolic processes are likely to have an influence on ionic species and mineral precipitation in the meltwater ponds included in this study.

These three processes, one physical, one chemical and one biological, essentially create disequilibrium within the meltwater pond system which fundamentally differs from the equilibrium conditions modelled by FREZCHEM. The comparison of water samples collected from meltwater ponds during the Antarctic summer (December 2005 and January 2007 samples) and during freezing (February – April 2008 samples) with mineral precipitation and brine chemistry predicted using FREZCHEM62 enables the importance of these limitations when applying FREZCHEM62 to be assessed.

The following summarises the main discrepancies found between field measurements and FREZCHEM62 modelled results:

- Although the majority of minerals predicted to occur in the ponds were found in the field area, predictions for individual ponds did not always agree with the salts observed. This may be due to the permanent removal of specific mineral forming ions from the solution leaving the existing solution (on which the modelling is based) relatively depleted in those ions.
- Sylvite (KCl) was predicted to occur in several meltwater ponds but this has yet to be observed in field samples.
- FREZCHEM62 modelling is based on constant temperature decrements during freezing and a small decrease in temperature can result in the majority of the solution freezing. This differs significantly from the physical process of freezing observed in the field where meltwater ponds may show thermal variation with depth, with freezing occurring at the pond surface due to cold air temperatures but remain above 0˚C at the base of the pond (see Chapter 3).
- FREZCHEM62 requires residual fluid to be present in order to converge; however, research suggests that some meltwater ponds freeze solid during winter with no residual water phase.

5.5 Conclusions

Although there are some significant limitations to the FREZCHEM62 model, namely the inherent disequilibrium that is present not only in meltwater ponds but in all natural environments, overall this type of chemical equilibrium modelling provides a reasonable approximation of many of the

chemical processes occurring during meltwater ponds freezing and evaporation. Therefore, the FREZCHEM62 model is a valid tool for predicting the brine chemistry during the extreme winter period when field sampling is logistically difficult.

Comparisons between actual basal brines that developed in Bratina Island meltwater ponds during freezing and FREZCHEM62 modelled brine compositions for the equivalent degree of freezing (as approximated by % ice volume) yielded similar results with ratios between actual and modelled concentrations near 1. This model validation means that FREZCHEM62 results can be accepted with greater confidence. Importantly, the most consistent field and modelled results were for P70 Pond, a pond that is known to be fully mixed during the summer period (due to the high visibility in this pond the lack of basal brine is easily identified) and therefore bulk pond compositions were potentially more accurate. This comparison also indicated that over prediction of carbonate, specifically dolomite, may occur in some instances (as in Skua Pond and Orange Pond).

FREZCHEM62 predictions of brine evolution in meltwater ponds during freezing indicated early precipitation of $CaMg(CO_3)_2$, $Na_2SO_4.10H_2O$ and in some instances $MgCO_3$ and $CaSO_4.2H_2O$ with $NaCl.2H_2O$, $CaCO_3$, $NaHCO_3$, KCl and $MgCl_2.12.H_2O$ precipitating as the models eutectic point was reached corresponding well to the types of salts identified in field samples. Of the 9 minerals predicted to precipitate at least 5 (possibly 7) were observed in sediment and salt samples from the Bratina Island area. Sylvite (KCl) was predicted to precipitate at or near the eutectic temperature in four ponds (Upper, P70, P70E and Skua) but as yet has not been identified in field samples, possibly due to a lack of samples collected from brines so close to their eutectic point (if they in fact reach that during freezing). This research is the first time that the evaporative regime of the FREZCHEM62 model has been used for Bratina Island ponds and predicted minerals were consistent with those found. Therefore FREZCHEM62 is valuable as a qualitative tool to determine the types of minerals that may be present at the base of Bratina Island meltwater ponds during winter.

Given the logistical constraints that are associated with Antarctic field work outside of the summer months between November and February, FREZCHEM62 is an effective tool with which to estimate winter conditions in meltwater ponds. In summary, the following measures would give the greatest accuracy when using FREZCHEM62 to predict winter meltwater pond chemistry:

- Base calculated bulk pond compositions on fully melted mid or late summer pond compositions rather than conditions immediately post melting.

- All ponds for which winter brine prediction is intended should be first profiled using a conductivity meter and then water samples collected from representative depths to take into account the heterogeneous nature of meltwater ponds.
- Ideally select study ponds for winter brine composition predictions that are fully mixed in summer as bulk pond chemistry calculations appear to be more accurate.
- If possible, a detailed bathymetry of each study pond (especially those that are stratified) combined with water sampling through the water column would yield more accurate bulk pond chemistry calculations.
- As stratification appears to be overturned by convection during freezing, both stratified and non stratified ponds can be treated the same when predicting winter brine compositions.
- Accept predictions of sylvite precipitation cautiously as this mineral has not yet been identified in field samples.
- Unexpectedly low concentrations of HCO_3 in modelled results may be the result of carbonate mineral (e.g. dolomite) over prediction.
- Further validation in the form of empirical modelling and laboratory experiments of the brine formation process would also improve the reliability of FREZCHEM62 particularly if it is to be used for quantitative analysis.

Further investigation is needed into the potential influence of microbial communities on the chemical conditions in meltwater ponds and the potential for biological processes to influence predictions of winter brine chemistries, as will be covered in the subsequent chapter.

CHAPTER 6

THE EFFECTS OF BIOTA ON MAJOR ION CHEMISTRY IN MELTWATER PONDS

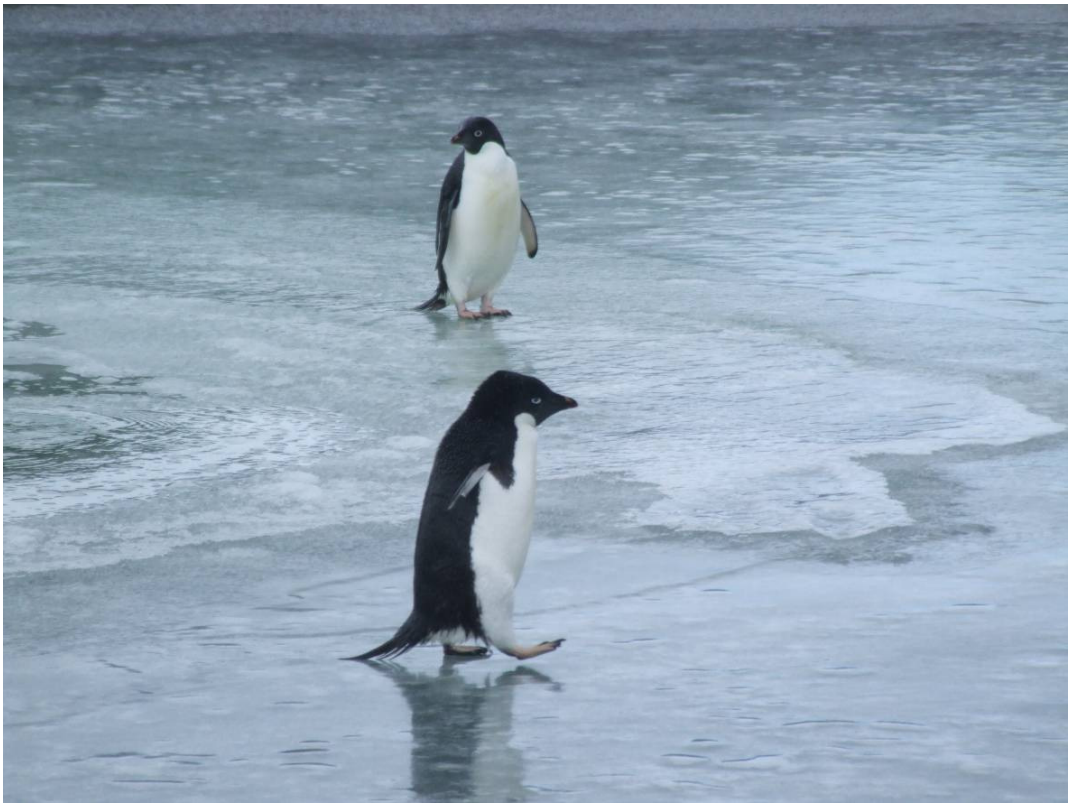

Figure 6. A pair of Adélie penguins walking on the surface ice of a frozen meltwater pond a long way from home (December 2005).

This chapter looks at the distribution of nutrients in both the stratified and mixed meltwater pond environment and the relative importance of the associated biogeochemical processes on major ion concentrations during the thaw, summer and freezing phases. Additionally, this Chapter identifies potential exchanges between inorganic and organic nitrogen, phosphorus, carbon and sulfur ions and the implications that these exchanges may have on attempts to understand and model the major ion chemistry of the meltwater pond system, particularly during winter.

6.1 Context of this Research

The biological components of ecosystems are built from elements in proportions that are usually strikingly different to how they occur in the abiotic ecosystem. Carbon is typically the dominant element at *c.* 40% of organism mass, while nitrogen (4%) and phosphorus (0.4%) are typically also disproportionately high compared to the environment and complex physiological mechanisms have been evolved over time to accumulate these essential elements despite low ambient concentrations. The major elements that are typically most abundant in the environment, such as sodium, calcium, magnesium, potassium, chloride, sulfate and bicarbonate, are required by organisms in relatively small amounts compared to the proportions in which they naturally occur, though all are ultimately obtained from external sources. Biological systems can therefore influence the geochemistry of a water body by taking up and releasing the solutes that they require for growth and metabolism through a range of metabolic processes, such as photosynthesis and respiration. In the context of this research, the question lies in how much influence do the biological systems have on the overall major ion chemistry of the meltwater ponds. The answer to this important question will determine whether the major ion geochemistry can be effectively described and conceptually modelled with or without consideration for the biochemical processes.

There are two communities of organisms within meltwater ponds that utilise and influence the biogeochemical cycling of nutrients; a planktonic and a benthic community (Parker & Simmons 1985). The most conspicuous components of the benthic community are thick mats of cyanobacteria, diatoms and other algae, which often form a complete cover over the sediments that line the ponds. The MIS is reportedly one of the largest concentrations of non-marine biota in the Ross Sea area, with biomass (as chlorophyll-a) in these ponds ranging from 80 – 641 mg m^{-2} (Howard-Williams *et al.* 1990; Hawes *et al.* 1993; Hawes *et al.* 1997), accumulated over many years (Hawes *et al.* 1993). Phytoplankton in MIS ponds contribute relatively little to this biomass, usually < 5 mg chlorophyll-a m^{-2}, generally attributed to the low inorganic nitrogen concentrations in the pond water (Hawes *et al.* 1993). For the purposes of this research, this chapter will focus on the benthic mat community only.

Freshwater environments in Antarctica offer a relatively simple ecosystem in which to investigate complex processes such as nutrient cycling due to a short food chain and the low activity of the herbivores and detritivores (Howard-Williams *et al.* 1989), which results in the microbial community playing a dominant role in nutrient cycling (Smith 1985). Nutrient availability varies seasonally with temperature, water availability and productivity; consequently, nutrient dynamics

of inland waters are dependant on coastal proximity, catchment characteristics, and the temperature and precipitation regime of the area (Smith 1985). Eight primary physical and chemical variables influential in regulating biological community structure and metabolic processes important to nutrient cycling have been identified in Antarctic lakes (Parker & Simmons 1985). These variables are also relevant to the meltwater pond environment and include (Parker & Simmons 1985):

- Degree of turbulence and mixing;
- light transmission through ice and water;
- temperature stability and range;
- salinity;
- the availability and concentration of dissolved oxygen;
- the availability of inorganic carbon;
- the availability of inorganic nitrogen; and
- the availability of dissolved reactive phosphorus (DRP).

In addition, seasonal changes in the ice cover in meltwater ponds, including the presence of an ice plug during melting, is very important in regulating biological processes as discussed in Chapter 3.

6.1.1 Nitrogen in the Meltwater Pond Environment

Dissolved inorganic nitrogen (DIN) refers to the dissolved concentrations of nitrate (NO_3), nitrite (NO_2) and ammonium (NH_4) combined. Analytically, NO_3 and NO_2 are often measured together, with NO_3 typically the dominant partner. The total dissolved nitrogen (TDN) concentration in a pond is DIN plus the concentration of dissolved organic nitrogen (DON). Although concentrations of dissolved inorganic nitrogen (DIN) are low in MIS meltwater ponds, DIN is a major component of meltwater ponds in other areas of Antarctica, such as in the Wright Valley, Victoria Land (e.g. Healy *et al.* 2006) and in the Darwin Glacier area (Vincent & Howard-Williams 1994).

Nitrogen is of biological significance to microbial communities in meltwater ponds and is an essential nutrient for growth. Antarctic meltwater ponds are the ideal locality to investigate nitrogen cycling as many of the biological, chemical and physical pathways between the different species of N that have been identified in ecosystems around the world have been identified in Antarctic inland waters (Howard-Williams & Hawes 2007). For example, there are significant

transformations from DIN to DON including N-uptake, N-fixation, N-release, ammonification, nitrification, denitrification, and dissimilatory nitrate reduction, and reaction rates can be similar to those at lower latitudes (Howard-Williams & Hawes 2007). The following chemical reactions, nitrogen fixation (Equation 6.1), the two stages of nitrification (Equation 6.2 and 6.3), and denitrification (Equation 6.4) illustrate the interaction between organic matter (CH_2O) and N and the conversion between the various species of N:

$$3CH_2O_{(s)} + 3H_2O_{(l)} + 2N_{2(g)} + 4H^+_{(aq)} \rightarrow 3CO_{2(g)} + 4NH_4^+{}_{(aq)} \quad \textbf{Equation 6.1}$$

$$2NH_4^+{}_{(aq)} + 3O_{2(g)} + 2H_2O_{(l)} \rightarrow 2NO_2^-{}_{(aq)} + 4H_3O^+_{(aq)} \quad \textbf{Equation 6.2}$$

$$2NO_2^-{}_{(aq)} + O_{2(g)} \rightarrow 2NO_3^-{}_{(aq)} \quad \textbf{Equation 6.3}$$

$$4NO_3^-{}_{(aq)} + 5CH_2O_{(s)} + 4H_3O^+_{(aq)} \rightarrow 2N_{2(g)} + 5CO_{2(g)} + 22H_2O_{(l)} \quad \textbf{Equation 6.4}$$

Sources of N in isolated meltwater ponds included N-fixation, wind-blown dust, precipitation and basal ice melt (Downes *et al.* 2000; Hawes *et al.* 2008). Numerous authors have investigated aspects of N biogeochemical cycling in Antarctic meltwater ponds (e.g. Hawes *et al.* 1993; Vincent & Howard-Williams 1994; Downes *et al.* 2000; Quesada & Fernandez-Valiete 2000; Howard-Williams & Hawes 2007) and the streams feeding into meltwater ponds and lakes (e.g. Hawes & Brazier 1991; Howard-Williams *et al.* 1997; McKnight *et al.* 2004).

On the MIS most meltwater ponds are considered N-limited. Surface water samples from Bratina Island ponds on the MIS show low concentrations of DIN (median concentration of 21 µg L^{-1}; Hawes *et al.* 1993), therefore N inputs to these ponds are of great significance (Quesada & Fernández-Valiente 2000). Depletion of NO_3 was noted in small Bratina Island meltwater ponds over a 4 week period in January by James *et al.* (1995). The concentration of DIN is also low in Bratina Island ponds relative to organic nitrogen (Hawes *et al.* 1999) reflecting the predominantly marine source of salts and proximity to the coast (Howard-Williams *et al.* 1989; Quesada & Fernández-Valiente 2000). Despite low concentrations, it has been suggested that N in the water column of MIS ponds is in fact controlled by the amount released by benthic cyanobacterial mat communities and that N does not limit microbial mat growth due to internal recycling (Hawes *et al.* 1993).

In inland or continental Antarctica NO_3 is non-biogenic in origin instead being precipitated in snow and accumulating as surface snow sublimates (Smith 1985; Vincent & Howard-Williams 1994). As mentioned in Section 4.1.1, atmospheric or stratospheric aerosol salts such as HNO_3 and $(NH_4)_2SO_4$ are thought to be the original source of NO_3 and SO_4 in inland areas (Campbell & Claridge 1977, Vincent & Howard-Williams 1994). High NO_3 concentrations (e.g. up to 24400 µg kg^{-1}) were measured in inland meltwater pond systems in the Victoria Valley (Webster *et al.* 1994;

Healy *et al.* 2006) with high concentrations also found in the Darwin Glacier region (Timperley 1997).

6.1.2 Phosphorus Concentrations in Meltwater Ponds

Phosphorus is essential to all life as it provides the structural framework for deoxyribonucleic acid (DNA) and ribonucleic acid (RNA), transports cellular energy in the form of adenosine triphosphate (ATP), and is a major component of phospholipids that form cell membranes. Inorganic phosphorus, specifically dissolved reactive phosphorus (DRP) is not a major component of meltwater pond chemistry but, as P is an essential element required for all living cells, it is discussed here. The total dissolved phosphorus (TDP) concentration in a solution includes both the DRP and dissolved organic phosphorus (DOP).

In general, P enters aquatic systems via land and direct atmospheric deposition on water surfaces (Kalff 2002). In the Lake Bonney catchment in the MDV's, the principle source of inorganic P is in the form of leachate from weathered rocks, soil, glacial flour and sediment that is transported into the lake environment by streams (Smith 1985). It has also been proposed that apatite weathering is a key source of PO_4 (Green *et al.* 1998). In some coastal environments, for example Signy Island meltwater ponds, P may be high due to inputs from resident Skua populations (Smith 1985). In a previous study, meltwater ponds on the MIS were found to have moderately high DRP concentrations (median 34 mg m^{-3}) in the surface waters (Hawes *et al.* 1993).

The biological release of P can be an important process as it is estimated that between 10-75% of potentially soluble P in sediments is not sorbed but held within microbial cells. The release of P depends on DO concentrations (at low DO sorbed phosphate tends to be released) and on the supply of P in sedimenting particles and the biological and chemical retention capacity (Kalff 2002). The uptake and release of P is not exclusively a chemical or physical or biological process as dissolved P is less able to be taken up by sediments in the absence of micro-organisms.

Phosphate (PO_4) is released in the oxidation of organic matter by aerobic and anaerobic micro-organisms. Assuming that C:N:P is equal to 106:16:1 in a micro-organism (the "Redfield ratios" often taken as typical of aquatic organisms), the following stoichiometry (Equation 6.5) illustrates PO_4 dynamics during aerobic decomposition and growth (Kalff 2002):

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138O_2 \leftrightarrow 106CO_2 + 16HNO_3 + H_3PO_4 + 122H_2O$$

Equation 6.5

This relationship between C:N:P is important for life. Ratios of DIN:DRP are typically low in the water columns of MIS ponds (Howard-Williams *et al.* 1989; Howard-Williams *et al.* 1990) though this is not reflected by N deficiency in the pond mats. There, C:N ratios of generally <20:1, are not indicative of N being in short supply for growth (Howard-Williams *et al.* 1989). The ratio of N:P only becomes important when one of these elements becomes limiting to growth.

6.1.3 Carbon in the Meltwater Pond Environment

Dissolved inorganic carbon (DIC), in this case measured as bicarbonate (HCO_3), is an important major ion in meltwater ponds. The concentration and speciation of DIC (see Equations 6.6, 6.7, 6.8 and 6.9) plays an integral role in the precipitation of carbonate minerals, due to the limited solubility of CO_2. The speciation of DIC is also important as organisms utilise specific forms of carbon (C); for example, the DIC species are differentially utilised in photosynthesis as carbon sources for the growth of primary producers.

$$CO_{2(gas)} \leftrightarrow CO_{2(dissolved)} \quad \textbf{Equation 6.6}$$

$$CO_{2(dissolved)} + H_2O \leftrightarrow H_2CO_3 \quad \textbf{Equation 6.7}$$

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+ \quad \textbf{Equation 6.8}$$

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \quad \textbf{Equation 6.9}$$

Biological activity can therefore influence the concentration of HCO_3 and alter the pH of an environment through the uptake and fixation of CO_2 during photosynthesis. In MIS ponds, low DIC (<15 mg L^{-1}) and high pH waters (>8) allow for little free CO_2 which is attributed to microbial uptake of DIC during photosynthesis (Hawes *et al.* 1993). Photosynthesis (Equation 6.11) initially consumes dissolved CO_2 and when this becomes depleted, converts HCO_3 to CO_2 (Equation 6.11), using the enzyme carbonic anhydrase to catalyse the transformation. As the CO_2 from the HCO_3 is consumed, the OH^- is released and the pH increases accordingly.

$$CO_2 + H_2O \rightarrow [CH_2O] + O_2 \quad \textbf{Equation 6.10}$$

$$HCO_3^- \rightarrow CO_2 + OH^- \quad \textbf{Equation 6.11}$$

When conditions of high pH and elevated photosynthetic activity prevail, the probability of CO_3 precipitating increases as the pH of the water rises (de Vrind - de Jong & de Vrind 1997). For example, calcite deposition is enhanced in the presence of supersaturated Ca, CO_3, and an alkaline pH. In Antarctic meltwater ponds this pH effect is strongly seasonal showing a contrast between the period during winter, when photosynthesis is absent and pH is relatively low, and the summer period when intense photosynthesis activity and relatively high pH prevail.

In addition, CO_3 minerals can be precipitated within the micro-environment of a cyanobacterial mat by the alteration of water chemistry. Supersaturated conditions can be reached by metabolic

alteration of HCO_3 and pH, and the availability of cells as nucleation sites can lead to precipitation (Little *et al.* 1997). This also has implications for the mineral species present in the surrounding environment. For example, during summer months when the rate of photosynthesis is highest, the pH of the surrounding environment can increase to >8, causing gypsum (which precipitates at a pH of approximately 8) to become unstable and convert to calcite (Fortin *et al.* 1997).

Sources of DOC in Antarctic terrestrial water bodies (e.g. lakes and ponds) include the breakdown of particulate organic C (Squyres *et al.* 1991; Priscu *et al.* 1998), phytoplankton primary productivity and DOC release (Priscu *et al.* 1999), and excretion and diffusion from benthic mat communities (Hawes & Schwarz 1999) and sediments (Tackecs *et al.* 2001). In MIS pond ecosystems, cyanobacterial mats are the principal source of DOC (Hawes *et al.* 1993).

Methane (CH_4) is also a key component of the C cycle that is produced primarily in anoxic sediments. In the anoxic basal waters of stratified Antarctic lakes it has been found that although CH_4 is an important diffusional flux of carbon from the sediments into the overlying water column, it is almost entirely utilised by aerobic processes (Smith *et al.* 1993). In MIS ponds, anaerobically generated CH_4 does not leave the mat environment during summer but is re-oxidised (Mountfort *et al.* 1999), while in winter CH_4 begins to accumulate in residual water (Ian Hawes, personal communication 2009). Concentrations of CH_4 in MIS pond sediments ranged from 0 to 3.5 mg kg^{-1} and tended to increase with increasing sediment depth with maximum concentrations occurring 16 cm below the sediment surface (Mountfort *et al.* 1999).

6.1.4 Sulfate Concentrations in Meltwater Ponds

Sulfate (SO_4) is a major ion in Antarctic inland waters, including meltwater ponds in coastal (Wait *et al.* 2006) and inland (Healy *et al.* 2006) environments. Sulfate is a major ion that can be strongly influenced by micro-organisms, as certain bacteria that are commonly associated with cyanobacterial mats reduce or oxidise sulfur by converting SO_4 to hydrogen sulfide (H_2S), or vice versa. This represents a shift between S with an oxidation state of +6 and S with an oxidation state of -2, which occurs primarily in reducing environments. For example, microbial SO_4 reduction uses SO_4 to release energy through oxidation of carbohydrate to CO_2 and H_2S Equation 6.12).

$$2CH_2O_{(s)} + SO_4^{2-}{}_{(aq)} + 2H^+ \rightarrow 2CO_{2(g)} + H_2S_{(g)} + 2H_2O_{(l)} \qquad \text{Equation 6.12}$$

The presence of a H_2S smell was noted in the winter ice of several MIS ponds and was indicative of reduced conditions and SO_4 reduction, most likely resulting from biological processes (Wait *et al.* 2006). The development of anoxic conditions and the production of H_2S have also been attributed to the commencement of biological activity in Antarctic lakes (Vincent & Vincent 1982;

Webster 1994). Biologically mediated reactions can also result in the formation of elemental sulfur and many other sulfur compounds (Morse *et al.* 1987; de Mora *et al.* 1996). The anoxic environment beneath cyanobacterial mats can contain reduced sulfur gases (de Mora *et al.* 1990), while dimethylsufide or DMS ($(CH_3)_2S$) and carbon disulfide (CS_2) have been identified in pond waters (Shooter *et al.* 1992). Consequently, the presence of SO_4-reducing bacteria in the cyanobacterial mats, if sufficiently active, may influence the S chemistry of the meltwater pond environment. Sulfate reduction is also an important terminal anaerobic process operating in the sediments at the base of meltwater ponds on the MIS (Mountfort *et al.* 1999). In high-SO_4, unfrozen sediments, C flow was found to be almost entirely mediated by SO_4 reduction (Mountfort *et al.* 2003).

The redox potential (Eh) of an environment is a composite measure of the balance between oxidising and reducing processes and S is important in determining the redox potential of an environment via the S(+6)/S(-2) redox couple. The oxidation reduction (redox) reaction for S is given below in Equation 6.13.

$$SO_4^{2-} + 8e^- + 10H^+ \leftrightarrow H_2S_{(aq)} + 4H_2O \qquad \textbf{Equation 6.13}$$

Redox reactions have a major effect on the concentration and/or form of organic C, DO, N, S, Fe, Mn and, to a lesser extent trace metals (Kalff 2002). Redox reactions are responsible for the oxidation of organic matter, nutrient cycling and the flow of energy between different trophic levels (Kalff 2002). Because redox reactions involve inorganic nutrients, the redox conditions in an aquatic environment can have a significant impact on the distribution of biota and determine whether particular nutrients are available for biological use; conversely, redox reactions are largely catalysed by micro-organisms.

6.1.5 Contribution of this Research

The intent of this research chapter is to consider the potential influence that biological interactions may have on predictions of winter meltwater pond chemistry. Nutrient samples from Bratina Island ponds have previously been collected from the surface water only, therefore an investigation into the distribution and concentration of various nutrients in meltwater ponds will be required before biological influence on pond composition can be assessed.

With the identification of strong chemical gradients and persistent stratification in meltwater ponds both coastal (Wait et al. 2006) and inland (Healy et al. 2006), it is unlikely that nutrient concentrations are homogeneous with depth. Additionally, the interactions between inorganic and organic species of N, P, C and S in the meltwater pond environment are examined as, until now, the organic and inorganic components of meltwater pond chemistry have largely been

considered separately. In order to fully understand and model either of these components, in this case the inorganic major ion chemistry of the ponds (as discussed in Chapters 4 and 5), the potential interactions between the biological and geochemical systems needs to be considered.

The first objective of this research is to identify concentration trends of N, P, C and S with depth in meltwater ponds in order to determine keyphysical, chemical and biotic factors influencing the distribution of these 'biologically influenced' ions in the water column.

The second objective of this research is to identify the biotic processes that may affect the concentrations of inorganic ions, specifically DIN, DRP, HCO_3, SO_4 and H_2S, in meltwater pond systems and to assess the relative importance of biological processes on the major ion chemistry of meltwater ponds. This will address a key limitation of using geochemical modelling to predict winter brine chemistry from summer meltwater pond compositions (as identified in Chapter 5).

Finally, factors controlling redox conditions in meltwater ponds and their brines will be identified focusing on the S(-2)/S(+6) and O(-2)/O(0) redox couples which can impact mineral precipitation and dissolution.

6.2 Data Collection & Analysis

Field measurements and water samples were collected from selected meltwater ponds in December 2005 and January 2007 as described in Chapter 2.2. Water samples were preserved and analysed for H_2S, dissolved species of nitrogen (NO_3^-, NH_4^+, TDN and DON) and phosphorus (DRP, DOP, TDP), as well as DOC. Laboratory methodologies used for sample analysis are described in Chapter 2.3.

The geochemical model PHREEQC (described in Chapter 2.4.1) was used to determine theoretical values of redox potential based on individual redox pairs as discussed later in this chapter (Section 6.4.7).

6.3 Results

6.3.1 Nutrient Concentrations in Meltwater Ponds

The concentrations of nutrients in the meltwater ponds, including NO_3, NH_4, TDN, DON, DIC, TDP, DRP and DOP, are shown in Table 6.1 and Table 6.2 for the 2005 and 2007 sampling seasons respectively. The results for each of the ponds that were stratified at the time of sampling are discussed individually below describing the changes in nutrient concentration that occurred with depth.

Table 6.1 Nutrient chemistry of Bratina Island Meltwater Ponds in December 2005 (italicised columns, DON and DOP, were calculated based on the difference between TDN and DIN, and TDP and DRP respectively).

Pond	Height above Sediment	NO_3-N	NH_4-N	*DON*	TDN	DOC	DRP	*DOP*	TDP	H_2S
2005	cm	µg L^{-1}	µg L^{-1}	*µg L^{-1}*	µg L^{-1}	mg kg^{-1}	µg L^{-1}	*µg L^{-1}*	µg L^{-1}	mg kg^{-1}
Upper	42	4	9	*4000*	4010	32.2	60	*172*	232	0.049
	27	3	31	*6060*	6090	61.2	264	*325*	589	nd
	17	5	28	*5750*	5780	73.8	343	*337*	680	nd
	7	21	48	*20200*	20300	157	1090	*760*	1850	nd
	1	23	391	*33600*	34000	329	2400	*1420*	3820	0.200
Huey	30	102	40	*1730*	1870	12.3	2	*38*	40	nd
	10	55	626	*8040*	8720	67.4	14	*130*	144	nd
	5	20	5570	*27600*	33200	254	555	*605*	1160	10.5
	1	14	8100	*42700*	50800	309	566	*804*	1370	14.8
P70	46	10	3	*1440*	1450	16.9	4	*43*	47	nd
	11	16	15	*1480*	1510	20.1	5	*39*	44	nd
	6	6	20	*2010*	2040	18.9	3	*51*	54	nd
	1	4	76	*36600*	36700	428	21	*599*	620	nd
P70E	46	9	7	*900*	916	7.6	3	*22*	25	nd
	26	8	5	*938*	951	9.0	4	*21*	25	nd
	16	11	19	*3110*	3140	35.2	13	*46*	59	nd
	6	6	68	*4270*	4340	57.2	24	*61*	85	nd
	1	7	84	*12000*	12100	110	20	*190*	210	nd

Upper Pond

The concentrations of DOC at the base of Upper Pond were very similar (329 and 316 mg kg^{-1}) between 2005 and 2007. Bicarbonate showed a slight increase from 2330 mg kg^{-1} in 2005 to 2881 mg kg^{-1} in 2007. In both 2005 and 2007, DON made up the majority (94-99%) of TDN in the pond. In 2005, NH_4 exceeded NO_3 throughout the whole profile and in the basal brine NH_4 was an order of magnitude higher than NO_3- (391 µg L^{-1} vs. 23 µg L^{-1}). In 2007, NO_3 exceeded NH_4 in the mixed surface layer but decreased (from 93 µg L^{-1} to 23 µg L^{-1}) at the top of the brine layer where NH_4 became dominant. The concentration of TDP dropped slightly between 2005 and 2007 with concentrations of 3820 µg L^{-1} and 3520 µg L^{-1} in the basal brine respectively. In 2005, DOP greatly exceeded DRP throughout the whole profile, although DRP did increase towards the base of the pond. In 2007, DOP exceeded DRP in the surface water only and showed similar concentrations in the basal brine.

Overall, in 2005 the nutrient concentrations in Upper Pond followed the same trend as Cl concentration and conductivity (see results tables in Sections 4.3.1 and 4.3.2 in Chapter 4). In 2007, nutrients showed the same conservative profile as Cl with the exception of TDN, DON and NO_3 as mentioned.

Table 6.2 Nutrient chemistry of Bratina Island Meltwater Ponds in January 2007 (italicised columns, DON and DOP, were calculated based on the difference between TDN and DIN, and TDP and DRP respectively).

Pond	Height above Sediment	NO_3-N	NH_4-N	*DON*	TDN	DOC	DRP	*DOP*	TDP	H_2S
2007	cm	µg L^{-1}	µg L^{-1}	*µg L^{-1}*	µg L^{-1}	mg kg^{-1}	µg L^{-1}	*µg L^{-1}*	µg L^{-1}	mg kg^{-1}
Upper	48	91	66	*3060*	3220	23.7	93	*168*	261	nd
	18	1	162	*2620*	2780	154	741	*709*	1450	0.002
	3	22	291	*32100*	32400	316	1850	*1670*	3520	0.103
Huey	28	40	59	*1910*	2010	21.8	<1	*47*	47	nd
P70	93	<1	5	*1950*	1950	26.2	13	*60*	73	nd
	53	<1	17	*1930*	1950	28.8	15	*61*	76	nd
	3	<1	15	*2010*	2020	27.5	13	*62*	75	nd
P70E	61	11	2	*1030*	1040	11.9	<1	*24*	24	nd
	3	3	88	*7570*	7660	81.1	<1	*142*	142	nd
Orange	78	7	55	*2070*	2130	21.0	7	*95*	102	nd
	8	<1	135	*4710*	4840	93.4	68	*338*	406	0.105
	3	<1	601	*38100*	38700	640	180	*1380*	1560	0.325
VXE6	62	2	19	*1780*	1800	19.9	<1	*41*	41	nd
	7	2	84	*8090*	8170	78.8	<1	*154*	154	nd
	3	4	97	*4370*	4470	127	<1	*210*	210	0.016
Egg-timer	104	2	123	*6500*	6620	13.9	18	*189*	207	nd
	24	3	239	*189*	431	108	<1	*346*	346	0.057
	14	7	8	*921*	935	193	<1	*26*	26	0.064
	3	<1	270	*24500*	24800	406	<1	*455*	455	0.056

P70E Pond

The concentration of DOC decreased slightly between 2005 and 2007 from 110 mg L^{-1} to 81.1 mg L^{-1}, HCO_3 also decreased from 270 mg kg^{-1} to 66.3 mg kg^{-1}. TDP was equal to DOP in 2007 with no detectable DRP present in the samples. TDP concentrations decreased between 2005 and 2007 from 210 µg L^{-1} to 142 µg L^{-1} (however Cl concentrations approximately halved during that period dropping from 28600 mg kg^{-1} to 13900 mg kg^{-1} as a result of an increase in water

depth and pond volume, Section 4.3.1 and 4.3.2). TDN decreased between 2005 and 2007 in the basal brine with concentrations falling from 12100 µg L^{-1} to 7660 µg L^{-1}, while concentrations increased slightly at the ponds surface. NO_3 and NH_4 concentrations remained similar throughout the water column between 2005 and 2007 with DON accounting for most of the change in TDN.

In 2005 and 2007 some of the nutrient concentrations behaved conservatively and followed the trend in Cl concentration (Section 4.3.2, Chapter 4) and conductivity while others did not - particularly NO_3, NH_4 and DRP in 2005 and NO_3, NH_4 and HCO_3 in 2007.

P70 Pond (stratified in 2005 only)

The key change that occurred between 2005 and 2007 in P70 Pond is the loss of stratification in the water column (as discussed in Chapter 4) and this is reflected in the nutrient concentrations. In 2005 the basal brine showed significant concentrations of TDN (36700 µg L^{-1}), DON (36620 µg L^{-1}), DOC (428 mg kg^{-1}), TDP (620 µg L^{-1}) and DOP (599 µg L^{-1}) which all drop by an order of magnitude in 2007. Conversely, the surface water layer generally increased in nutrient concentrations between 2005 and 2007 as the concentrated brine was dispersed throughout the water column. Nitrate and NH_4 decreased between 2005 and 2007 with NO_3 dropping to less than 1 µg L^{-1}.

In 2005 nutrient concentrations generally behaved conservatively (i.e. following the trend in Cl concentration with depth, Section 4.3.2, Chapter 4) with the exception of NO_3, NH_4 and DRP. In 2007 the pond was fully mixed with similar concentrations of all parameters at all depths, except NO_3 and NH_4 which varied throughout the water column.

Huey Pond (stratified in 2005 only)

All parameters behaved conservatively with depth in 2005 following the same concentration trend as Cl (i.e. increasing with depth, Section 4.3.2, Chapter 4), with the exception of NO_3 which decreased with depth (from 104 µg L^{-1} to 14 µg L^{-1}). In 2007, concentrations were very similar to the concentrations measured at the surface of Huey Pond in 2005 with a few exceptions; DRP that had been present in 2005 was below detection limits in 2007 and the concentration of NO_3 had halved.

Eggtimer Pond (2007 only)

There is a significant decrease in both TDN and DON at the top of the basal brine layer which then increase by two orders of magnitude at the base of the pond. Similarly, NH_4-N, DOP and

TDP showed a decrease in the middle of the basal brine layer but comparable concentrations throughout the rest of the water column including the basal brine. All other nutrients followed the same trend as conductivity and Cl concentration (Section 4.3.1 and 4.3.2, Chapter 4) and showed increased concentrations with depth.

VXE6 Pond (2007 only)

All nutrient concentrations, except HCO_3, TDN and DON, showed an increase with depth, particularly in the basal brine reflecting the conductivity of water. Bicarbonate, TDN and DON did not behave conservatively, instead showing a decrease in concentration in the brine layer. Despite the decrease TDN and DON concentrations were still greater that those measured in the mixed surface layer of the pond.

Orange (2007 only)

All nutrients in Orange Pond showed a conservative profile with concentrations showing approximately the same trend with depth as Cl and conductivity. There was a sharp increase in all nutrients in the brine layer.

6.3.2 Nutrient Concentrations in Ice Core

Table 6.3 Nutrient chemistry of Skua Pond (Bratina Island) ice core collected in October 2001.

Height above Sediment	Cl	NO_3	NH_4	DON	TDN	DOP	DRP	TDP
cm	mg kg^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	mg kg^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}
131	1.48	34	2	14	50	0	1	1
111	1.47	25	3	352	380	15	9	24
91	13	64	30	656	750	44	35	79
71	205	36	73	1240	1350	18	265	283
51	432	37	279	2790	3110	160	771	931
31	1050	79	845	3650	4580	0	1290	1290
16	4190	101	3740	19500	23300	526	8770	9300
6	5130	84	4180	18700	23000	349	8930	9280

Concentrations of the inorganic and organic forms of N and P taken from sections of Skua Pond ice core (sampled in October 2001) are shown alongside Cl concentrations in Table 6.3. Concentrations of NH_4, DRP and TDP increased with depth towards the base of the pond as did the concentrations of DON and TDN except in the basal ice layer. Concentrations of NO_3 varied with depth.

6.3.3 Redox Conditions

Measurements for DO and redox (Eh) at different depths in meltwater ponds sampled in December 2005 and January 2007 are shown in Table 6.4. In 2005 DO was strongly stratified in Upper Pond and Huey Pond with saturated conditions in the mixed surface layer of the pond decreasing to near anoxic conditions in the basal brine. DO was also stratified in P70 Pond and P70E Pond in 2005 however concentrations increased towards the base of the pond and were at or exceeding full saturation. In 2007, DO was reasonably constant through the water column at full saturation. Values for Eh in January 2007 indicate weak to moderately oxidising conditions in the ponds, with 4 out of 5 stratified ponds showing a slight increase in Eh towards the base of the pond.

Table 6.4 Dissolved oxygen and Eh measured in Bratina Island meltwater ponds in December 2005 and January 2007.

Pond	Height above Sediment	DO	Pond	Height above Sediment	DO	Eh
2005	cm	mg L^{-1}	2007	cm	mg L^{-1}	mV
Upper	42	13.9	Upper	48	12.6	319
	27	7.6		18	12.9	347
	17	4.7		3	12.7	361
	7	1.3	Huey	28	12.2	234
	1	1	P70	93		247
Huey	30	12.9		53		236
	10	6.2		3		240
	5	2.3	P70E	61	11.4	281
	1	1.27		3	12.6	255
P70	46	12.3*	Orange	78		232
	11	12.3*		8		245
	6	13.6*		3		244
	1	14.5*	VXE6	62	10.4	295
P70E	46	12.6		7		-
	26	15.8		3	12.0	274
	16	>20	Eggtimer	104	11.6	303
	6	16.8		24	11.1	330
	1	20		14		338
				3	14.1	345

* DO measurements were unable to be taken *in situ* for this sample; this result was measured in a pumped water sample and is likely to have undergone some degassing.

6.4 Discussion 1: Nutrient Concentrations in Meltwater Ponds

6.4.1 Nutrient Concentrations in Individual Meltwater Ponds

In the four stratified ponds sampled in December 2005, all nutrients except NO_3 showed an increase in concentration with depth, following a similar trend to that seen in major ion concentrations and conductivity (see Chapter 4). This suggests that freeze concentration has played a dominant role in the distribution of most elements within the pond as stratification at this point in time (soon after melting) should closely reflect the conditions set up during freezing. In 2005, concentrations of NH_4 in the two basal samples of Huey Pond were very high (5570 and 8100 mg m^3 5 cm and 1 cm above the sediment respectively) compared to the other ponds sampled, perhaps due to the rupture of microbial mats and subsequent release of DIN to the lower water column.

Trends were similar in 2007 to those seen in 2005. Most nutrient concentrations increased with depth in stratified ponds, with the exception of NO_3 which either decreased with depth (in Upper Pond and P70E Pond) and or showed little or no change with depth at low concentrations (Eggtimer Pond, Orange Pond and VXE6 Pond). With the exception of a single sample in Eggtimer Pond, concentrations of P appear to behave conservatively with depth showing an increase in concentration that parallels increases in conductivity. The same applies to concentrations of C (with the exception of a single sample at the very base of VXE6 Pond).

In some ponds, concentration changes were non-linear with depth. For example, in 2007 both Upper Pond and Eggtimer Pond (Figure 6.1) showed a decrease in the concentration of TDN and DON at the top of the basal brine layer but then concentrations increased once more at the base of the ponds. Eggtimer Pond (2007) also showed a decrease in TDP, DOP and NH_4 at mid depths in the brine layer before concentrations increased at the very base of the pond (Figure 6.1). At the very base of VXE6 Pond concentrations of TDN and DON approximately halved compared to the upper brine layer just 4 cm above. Deviation of nutrients concentrations away from conductivity trends could possibly indicate a planktonic community influencing concentrations at the boundary between the brine and the overlying water column.

No variation in the vertical distribution of nutrients was observed in P70 Pond in 2007, consistent with a well mixed water column. Huey Pond was also mixed in 2007 but as only a single sample was collected, change with depth cannot be interpreted. Concentrations of nutrients in the mixed sample were similar to those collected from the surface of Huey Pond in December 2005.

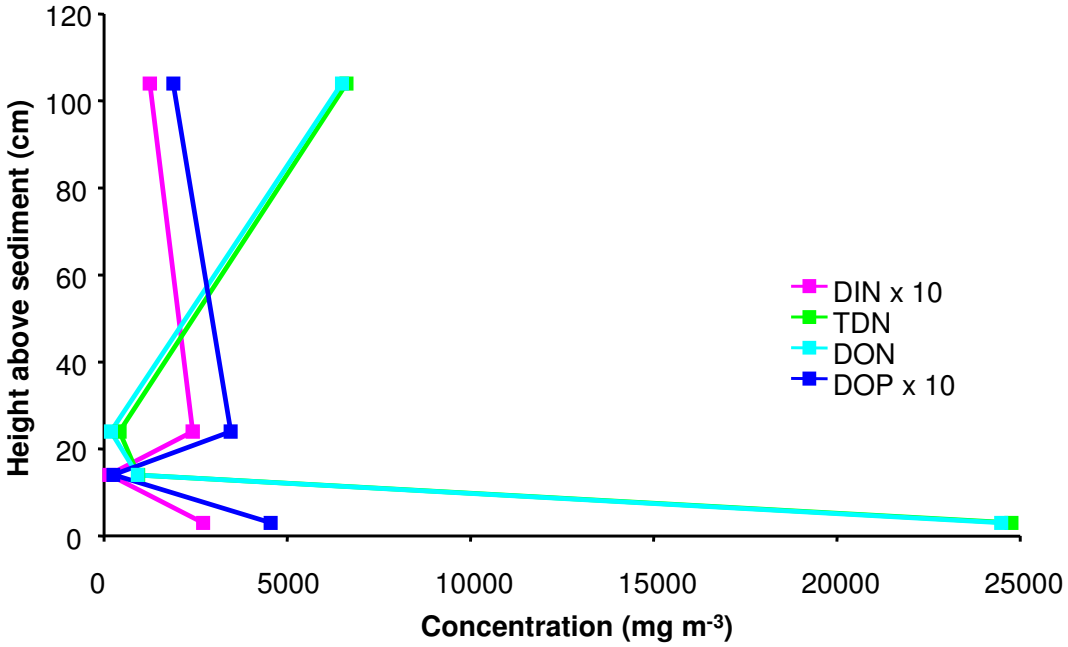

Figure 6.1 Concentration profiles with depth of NH_4, TDN, DON and DOP in Eggtimer Pond 2007. TDP is not shown but is equal in concentration to DOP in the three basal samples.

The various forms of inorganic and organic N show the least conservative behaviour of all the nutrients with depth, particularly NO_3 which shows no change or a decrease in concentration in the basal brines. The apparent loss of NO_3 in the basal layers is possibly the result of microbial denitrification under the low oxygen conditions present during the development of winter conditions, however in well oxygenated ponds mid-summer (January 2007 samples) NH_4 remained the dominant species of DIN and synthesis of NO_3 appeared slow.

The deviation of N away from conductivity has previously been noted in near-edge water samples from MIS ponds and was attributed to biological transformations (Hawes *et al.* 1993). Conversion of the large pools of NH_4 and DON to NO_3 could be accomplished by a variety of microbial processes, the dominant and final stage of which might be expected to be nitrification. Nitrification has been demonstrated in MIS ponds (see Downes *et al.* 2000; Howard-Williams & Hawes 2007) but does not appear to be quantitatively important in the brine layers of these ponds. There are several reasons why NO_3 may remain low, firstly there may be no new NO_3 produced as anoxic sediments (such as those beneath the mats) do not release NO_3 and there is no downward diffusion gradient to drive NO_3 into the brine layer from the mixed water column above. Secondly, high concentrations of DO can effect on the growth rate of nitrifying micro-organisms. In one study the uptake of O_2 was reduced when DO concentrations exceeded 15 mg L^{-1} suggesting that at this concentration DO may be toxic to nitrifying micro-organisms and thus nitrification is reduced (Jang & Kim 2004). Thirdly, nitrifying micro-organisms will be

competing against photosynthetic micro-organisms for CO_2 and nitrification may not be competitive, particularly at low DIC concentrations and alkaline conditions. Finally, the presence of sulfide can inhibit nitrification (Joye & Hollibaugh 1995).

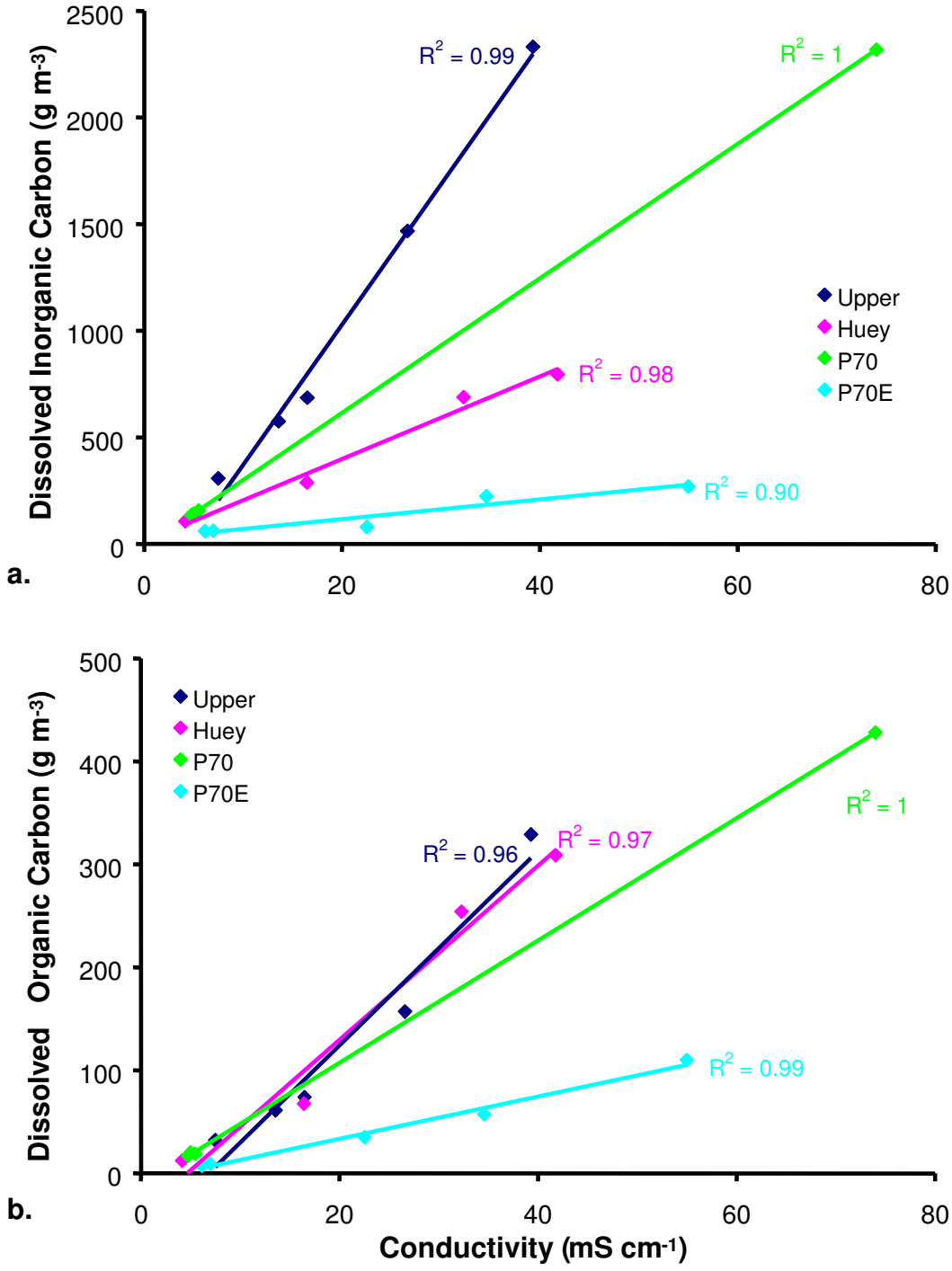

Figure 6.2 The relationship between a. dissolved inorganic carbon and conductivity and b. dissolved organic carbon and conductivity in meltwater ponds in December 2005.

Overall, there was little correlation between physical parameters and nutrient concentrations in individual ponds. No correlation was seen between the water temperature and pH at the time of sampling and the concentration of N, P or C in 2005 and 2007, which indicates that temperature and pH changes with depth had no effect on the nutrient distribution within the ponds. Similarly, DO and Eh showed no correlation with N, P and C concentrations. Instead, for almost all cases, the best linear correlation was between nutrient concentrations and conductivity.

For example, the concentrations of DOC and DIC show a positive correlation with conductivity in individual ponds sampled in December 2005 (Figure 6.2 a and b) and January 2007. In both 2005 and 2007, DOC had $R^2 > 0.96$ in each individual pond and DIC had $R^2 > 0.91$ with the exception of VXE6 Pond (2007) which showed no correlation between DIC and conductivity ($R^2 = 0.05$). The lack of correlation in VXE6 Pond most likely reflects the decrease in concentration of HCO_3 at the very base of the pond which does not occur in any other ponds sampled here. In general, the correlation between conductivity and nutrient concentrations indicate that both the inorganic and organic species of C within each pond are being driven by concentration effects.

Similar linear correlations were observed between conductivity and the concentrations of other nutrients in individual ponds which indicate that the physical processes effecting the distribution of major ions will primarily control the distribution of nutrients within that pond.

A key difference between the concentration of major ions and nutrients in meltwater ponds is that the major ions (Na, K, Mg, Ca, Cl, SO_4 and HCO_3) are present at significantly higher concentrations, typically several orders of magnitude, than the inorganic and organic species of N and P. In most cases HCO_3 concentrations (i.e. DIC) are also an order of magnitude greater than the concentration of DOC. Exceptions to this include samples from the base of P70E and VXE6 Ponds in 2007 where DOC exceeded the concentration of HCO_3.

6.4.2 Regional Variation in Nutrient concentrations

There was no overall correlation between conductivity and nutrient concentrations across all Bratina Island ponds included in this study. Figures 6.3, 6.4 and 6.5 illustrate this point by showing the lack of linear relationships between conductivity and the N, P and C species respectively. This highlights the fact that the major ion and nutrient composition of each meltwater pond is unique with no clear link between the nutrient and major ion concentrations that is applicable to all in Bratina Island ponds. Consequently, variables unique to each pond determine the major ion composition of the pond (Section 1.2.1) and the concentration of each of the nutrient species. Variation in nutrient concentrations may be the result of the following:

- The pond biomass (which can vary by a factor of 10; Hawes *et al.* 1993) and productivity;
- The amount of desiccated biomass in the pond catchment that may act as a source of nutrients to the pond;
- Inputs of nutrients to the ponds by birds (e.g. local Skua populations that nest in the area and the occasional penguin);
- The amount of mat rupture that may have released nutrients from the sediments in a pond;
- Freeze concentration of nutrients during winter (Howard-Williams *et al.* 1997) (as will be discussed in the following section); and
- Mineral precipitation and dissolution that may add or remove nutrients from the water column (e.g. the precipitation of carbonates and nitrates) (Howard-Williams *et al.* 1997).

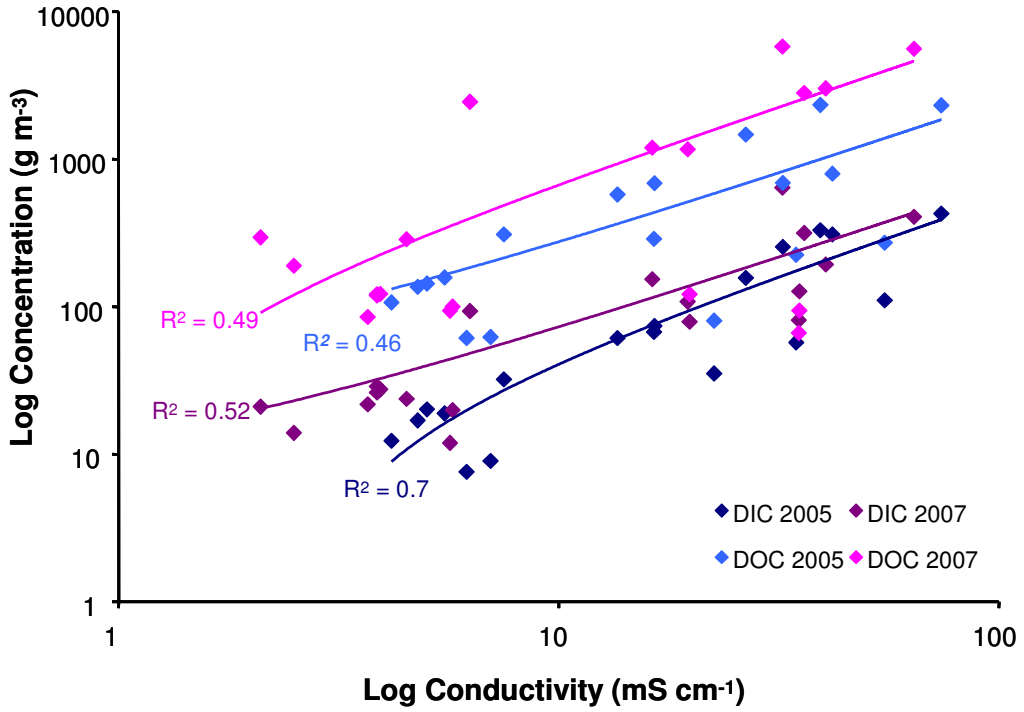

Figure 6.3 Correlation between carbon (DIC – bicarbonate and DOC) concentrations and conductivity in ponds on the MIS (2005 and 2007 data combined).

Some weak correlations were present when the inorganic and organic species of each nutrient were compared across all ponds. For example, Figure 6.6 shows a weak to moderate correlation between DIC and DOC in both years (2005: $R^2 = 0.76$, N = 18, P = 2.42×10^{-6}; 2007: $R^2 = 0.84$, N

= 21, P = 7.04 x 10^{-9}). In both years, there was no correlation between DON and DIN (Figure 6.7) (2005: R^2 = 0.43, N = 18, P = 0.003312; 2007: R^2 = 0.05, N = 21, P = 0.34797) and moderate correlation between DOP and DRP in 2005 only (Figure 6.9) (2005: R^2 = 0.83, N = 18, P = 1.83 x 10^{-7}; 2007: R^2 = 0.62, N = 21, P = 2.47 x 10^{-05}).

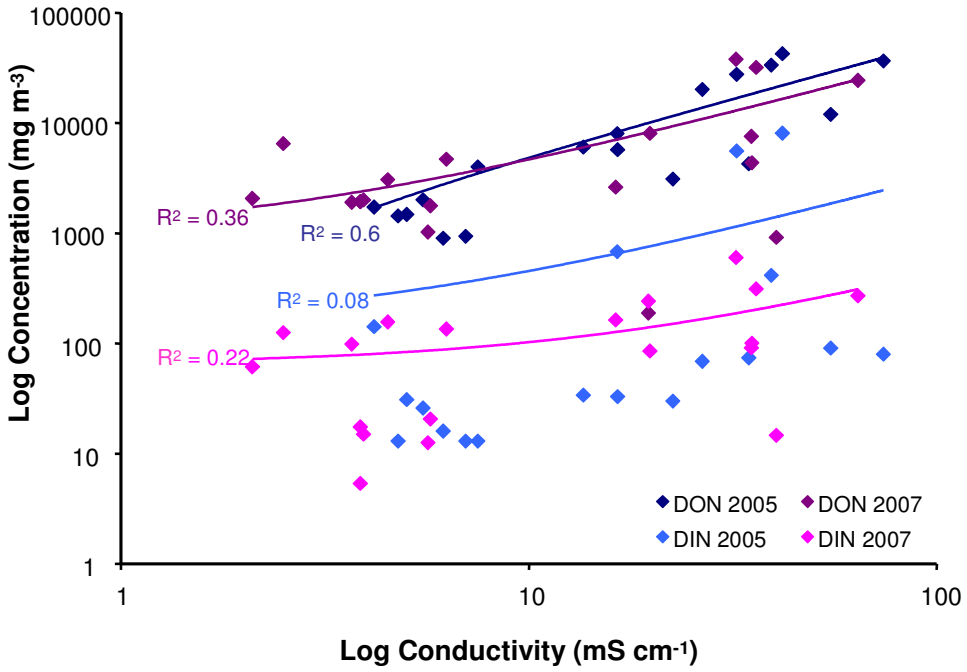

Figure 6.4 Correlation between Nitrogen (DON, NH_4 and NO_3) concentrations and conductivity in ponds on the MIS (2005 and 2007 data combined).

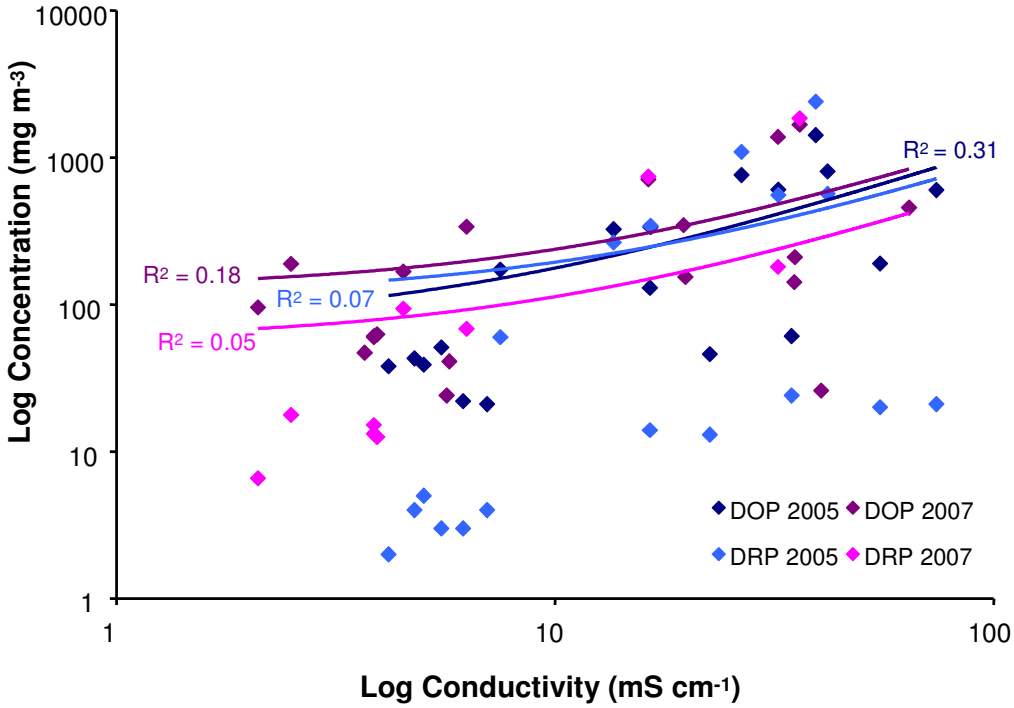

Figure 6.5 Correlation between phosphorus (TDP, DRP and DOP) concentrations and conductivity in ponds on the MIS (2005 and 2007 combined).

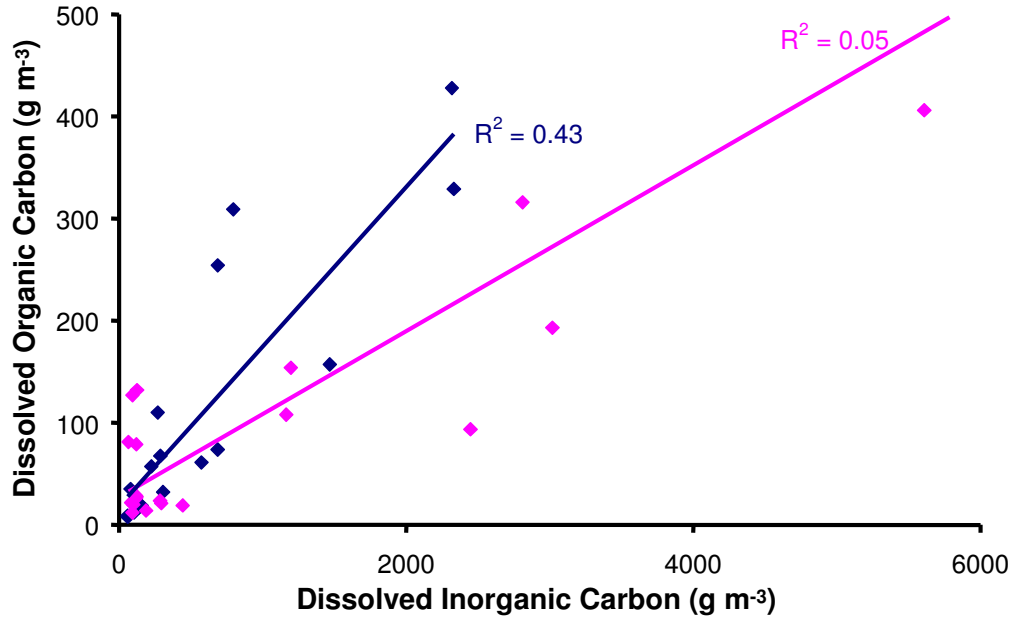

Figure 6.6 Correlation between DIC and DOC in meltwater ponds sampled in 2005 (blue) and 2007 (pink) showing corresponding linear trendlines and R^2 values.

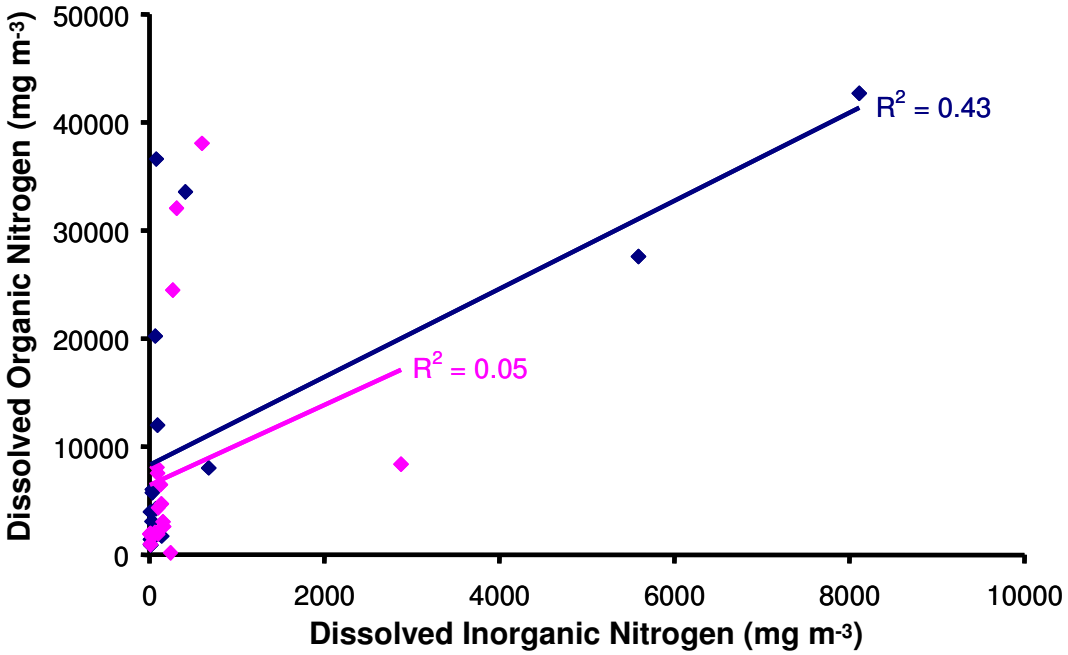

Figure 6.7 Correlation between DON and DIN in meltwater ponds sampled in 2005 (blue) and 2007 (pink) showing corresponding linear trendlines and R^2 values.

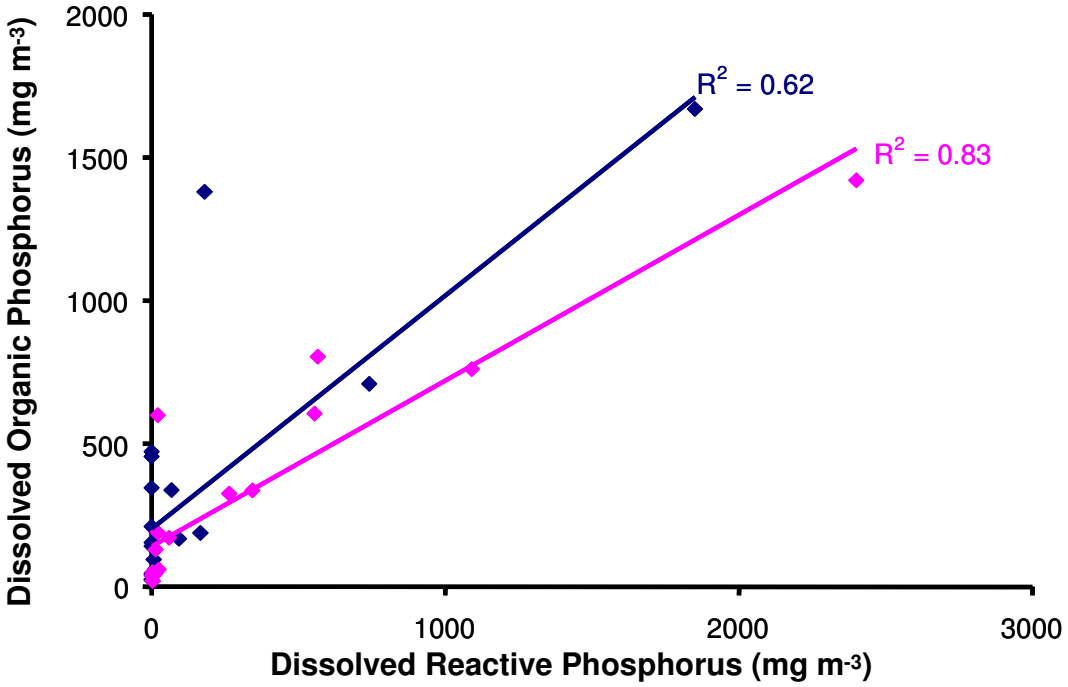

Figure 6.8 Correlation between DOP and DRP in meltwater ponds sampled in 2005 (blue) and 2007 (pink) showing corresponding linear trendlines and R^2 values.

6.4.3 The Influence of Freeze-Thaw on Nutrient Concentrations

Chemical stratification of meltwater ponds is a feature of the Bratina Island meltwater pond environment and is primarily set up by the process of freeze-thaw. During the freezing of meltwater ponds, dissolved salts are excluded from the newly forming ice at the surface of the pond and concentrated in the residual water phase resulting in the formation of saline brine at the base of the pond. This process of freeze concentration, the physical process of which is described in detail in Chapter 3, almost certainly plays a key role in determining the distribution of not only inorganic major ions as discussed in Chapter 4, but of nutrients as well, as indicated by correlations between conductivity and nutrient concentrations.

In order to understand how nutrient concentrations may be influenced by freeze concentration a comparison can be made between nutrient concentrations and the concentration of a conservative ion such as Cl, which is assumed to behave conservatively due to its high solubility, with increasing water depth. This relationship is shown in Figures 6.9 – 6.14 (graphs are not shown for TDN as it is almost identical to the graph for DON as the concentration of TDN is almost entirely comprised of DON, for the same reason TDP is not shown).

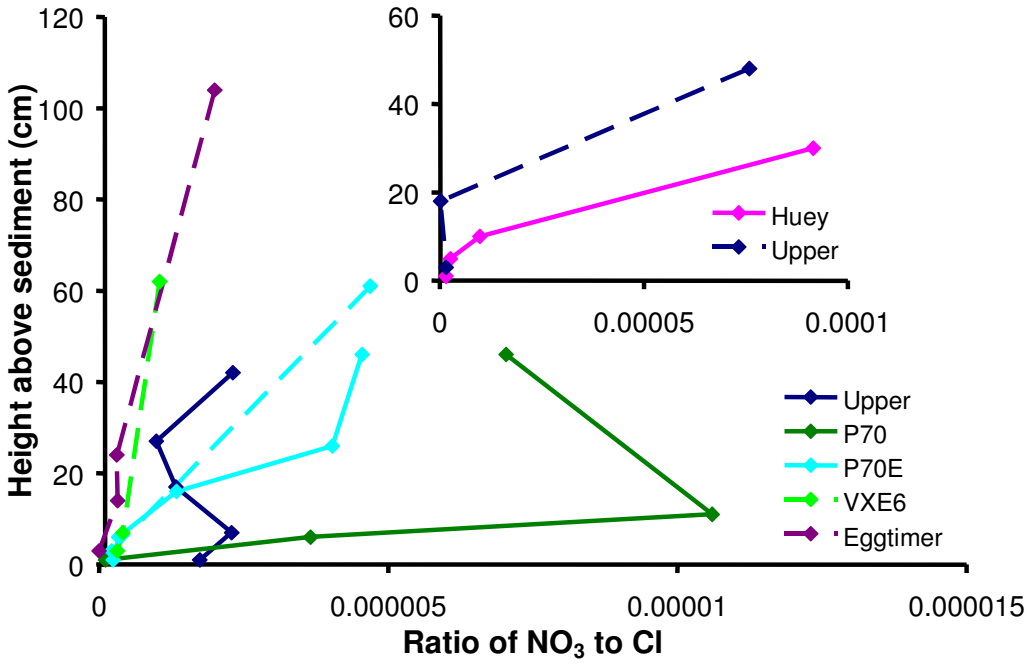

Figure 6.9 Graph showing the ratio of NO_3 to Cl versus depth in meltwater ponds sampled in 2005 (solid lines) and in 2007 (dashed lines). Both Huey Pond in 2005 and Upper Pond in 2007 had higher NO_3:Cl in the surface water than other ponds sampled (inset).

The NO_3:Cl ratio (shown in Figure 6.9) generally shows a decrease at the base of the ponds and was particularly significant in Huey Pond and Upper Pond in 2005 when the basal brine was anoxic. The ratio of NH_4:Cl shows a similar trend (Figure 6.10) except in the anoxic basal brine conditions of Huey Pond and Upper Pond in 2005 where NH_4 shows an increase relative to Cl. Dissolved organic nitrogen behaved fairly consistently compared to Cl in the upper water column (Figure 6.11). At the top of the basal brine both Eggtimer and Upper Ponds showed an order of magnitude decrease in the relationship to Cl, with higher ratios at the base of the pond. In the basal brine itself, there was no obvious trend in the DON:Cl ratio with some ponds increasing and other decreasing.

Dissolved organic carbon (Figure 6.12), DRP (Figure 6.13) and DOP (Figure 6.14) were reasonably conservative compared to Cl throughout the water column. At the base of Huey an increase in the ratio of all three of these parameters to Cl increased, while other ponds showed minor variation in the basal brine. Interestingly, Eggtimer Pond showed a decrease in the DOP:Cl ratio at the top of the basal brine very similar to that seen in the DON:Cl ratio. This suggests that some process, perhaps uptake by phytoplankton, is affecting both N and P in a similar way.

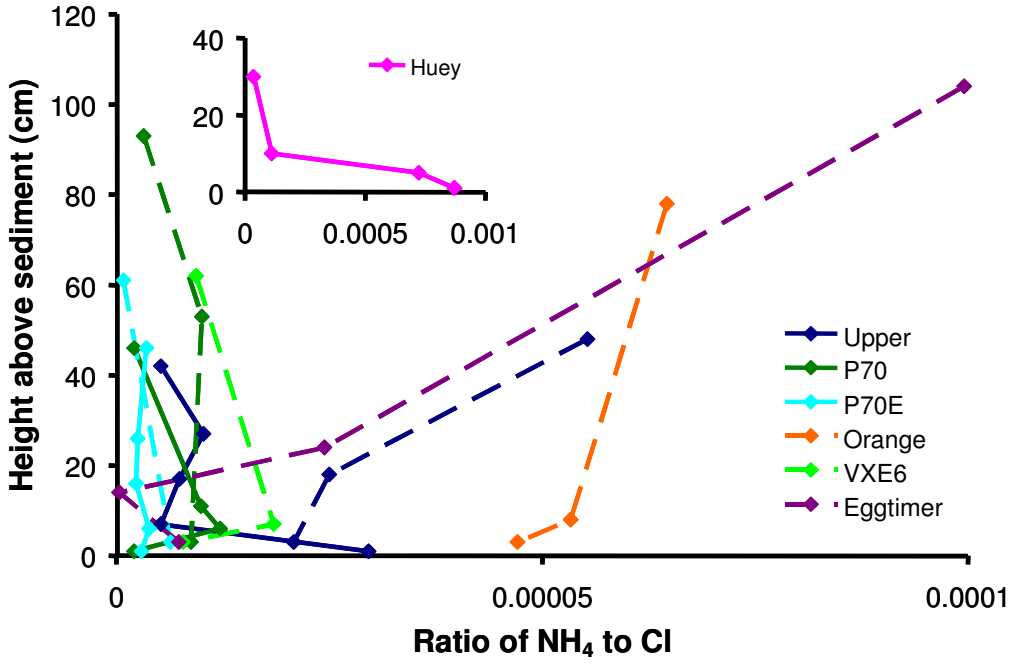

Figure 6.10 Graph showing the ratio of NH^4 to Cl versus depth in meltwater ponds sampled in 2005 (solid lines) and in 2007 (dashed lines). The inset graph illustrates the ratio of NH^4 to Cl in Huey Pond which was significantly higher in the two basal layers of the pond that in all other ponds sampled.

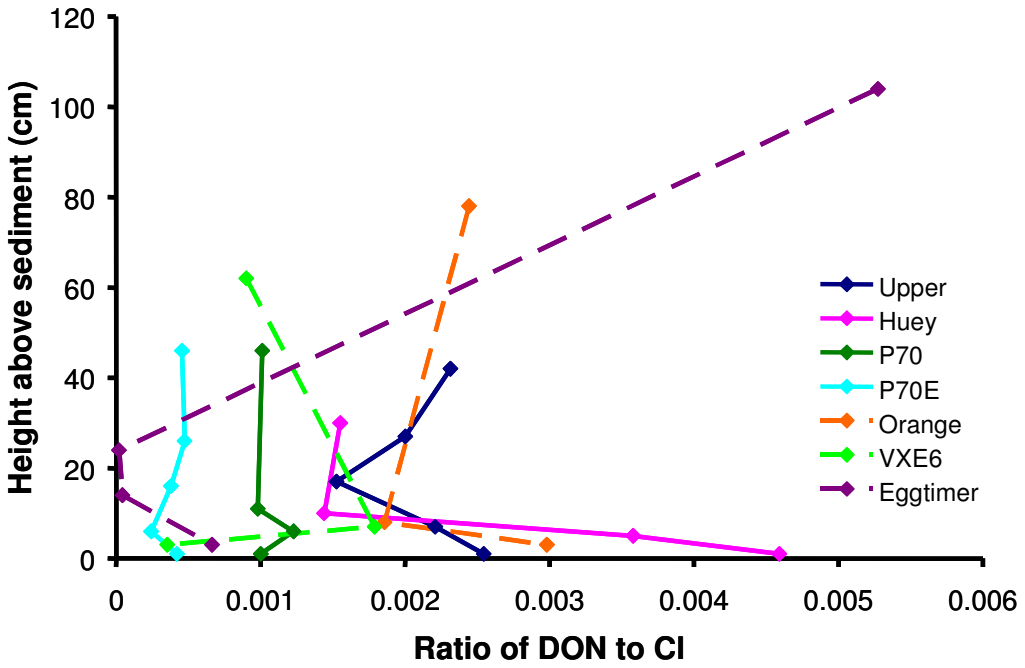

Figure 6.11 Graph showing the ratio of DON to Cl versus depth in meltwater ponds sampled in 2005 (solid lines) and in 2007 (dashed lines).

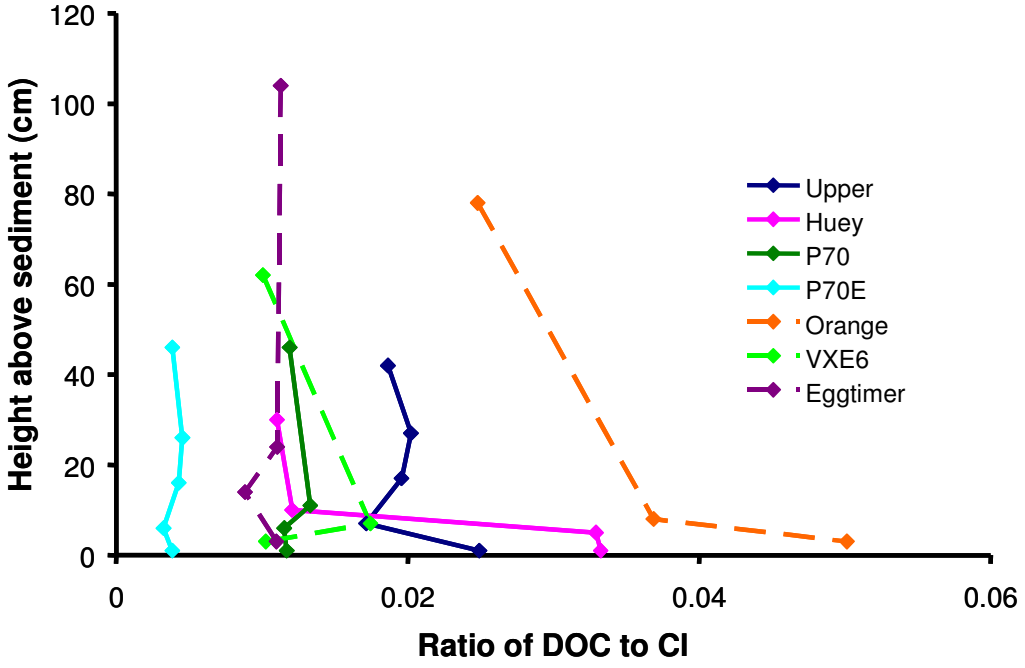

Figure 6.12 Graph showing the ratio of DOC to Cl versus depth in meltwater ponds sampled in 2005 (solid lines) and in 2007 (dashed lines).

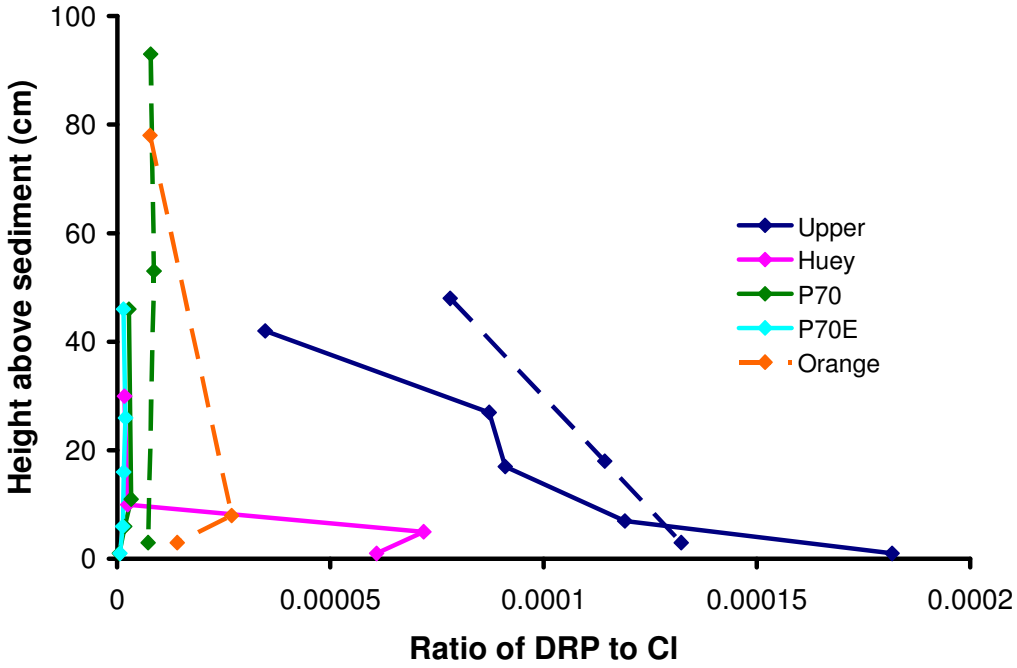

Figure 6.13 Graph showing the ratio of DRP to Cl versus depth in meltwater ponds sampled in 2005 (solid lines) and in 2007 (dashed lines).

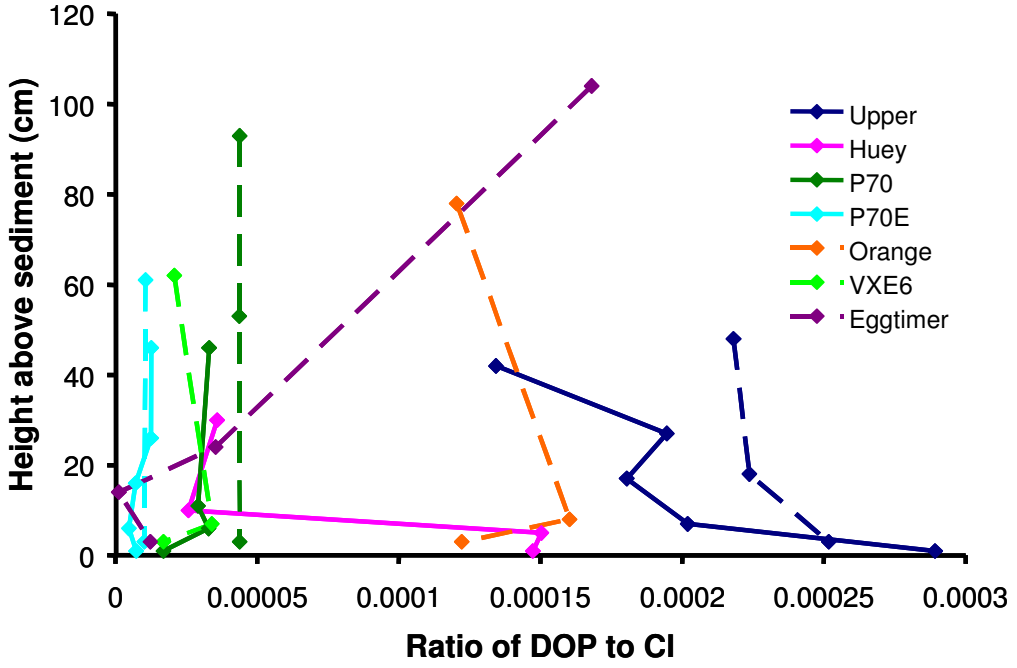

Figure 6.14 Graph showing the ratio of DOP to Cl versus depth in meltwater ponds sampled in 2005 (solid lines) and in 2007 (dashed lines).

In many of the Figures shown above, all but the basal water layers behave somewhat conservatively showing a constant ratio of nutrients to Cl with depth. This leads to the conclusion that the ponds can be separated into different sub units, with the basal layers that are isolated

from the overlying mixed water column behaving differently. In tidal lagoon ponds in Antarctica physical isolation of the deeper water layers away from the mixing zone is thought to be responsible for the depletion of nutrients and DIC, and the supersaturation of oxygen as a result of algal growth (Hawes *et al.* 1997). The same scenario is likely to occur in the ice shelf ponds investigated here. Consequently, the process of freeze - thaw is having a significant effect on the distribution of nutrients within the water column as the fluxes of nutrients to and from the benthic mat community at the base of the pond are isolated from the rest of the pond. This is illustrated by the restriction of H_2S to just the basal layers of the water column adjacent to microbial mats, that remain separated from the overlying mixed water column.

Overall, many of the nutrient concentrations appeared to behave conservatively within the ponds, generally increasing in proportion to conductivity and Cl concentrations. P70 Pond and Huey Pond were both well mixed in January 2007 and illustrate the fact that nutrients were well mixed also.

Nutrient Concentrations during Winter Freezing in a Mixed Pond

To investigate the relationship between freezing and nutrient concentrations, ice samples from Skua Pond were collected in October 2001 and analysed for nutrient concentrations as presented in Table 6.3. Skua Pond was most likely fully mixed prior to freezing as it is in an exposed catchment with a small inflow and outflow (see the location of Skua Pond in Figure 2.2) and stratification has not been identified in the summer sampling seasons since the ice core was taken. Figure 6.15 illustrates the ratio of each nutrient to Cl with depth.

Nutrients in the upper 60 cm of the ice core behave non-conservatively while the lower 70 cm of ice does. This 70 cm point may reflect the point at which biological photoautotrophic processes become restricted due to limited light conditions with the onset of winter darkness. Referring back to Figure 3.2 in Chapter 3, the point at which the upper 60cm of Skua pond became frozen occurred approximately 1000 hours (42 days) into the record (early April) coinciding with the point at which near complete darkness sets in. Consequently, non-conservative behaviours are likely to occur beneath the growing ice cover until photoautotrophic biota become inactive; likewise conservative behaviours indicate limited biological activity with physical processes controlling nutrient concentrations. The exception to this is the slight increase in NH_4 as NO_3 decreases most likely reflecting the decreasing availability of oxygen in the environment and the transformation from an oxygenated N species to a deoxygenated species.

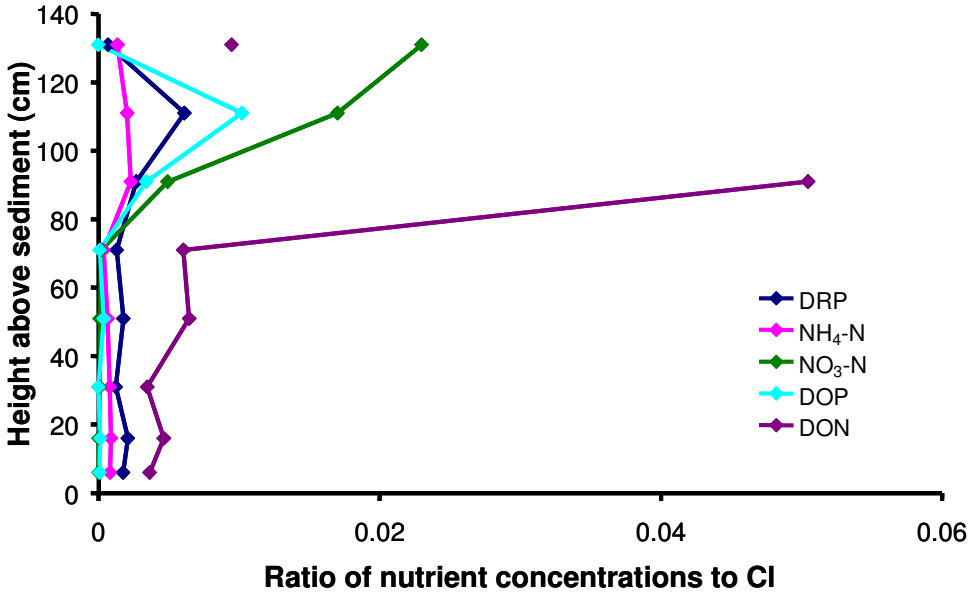

Figure 6.15 Graphs showing the ratio of nutrient concentrations to Cl concentrations in Skua Pond ice core collected in October 2001.

6.4.4 Calculated bulk pond nutrient chemistry

Table 6.5 Total concentration of nutrients in stratified ponds layers and total pond composition of selected meltwater ponds sampled December 2005.

Pond	Height above sediment	NO_3-N	NH_4-N	TDN	DON	DOC	TDP	DRP	DOP
	cm	mg	mg	mg	mg	g	mg	mg	mg
Upper	0.42-0.62	4.69	10. 6	4706	4691	37.8	272	70.4	202
	0.27-0.42	1.16	12.0	2354	2341	23.7	228	102	126
	0.17-0.27	0.525	2.94	607	603	7.75	71.4	36.0	35.4
	0.07-0.17	0.682	1.56	659	657	5.10	60.1	35.4	24.7
	0.01-0.07	0.056	0.950	82.6	81.62	0.799	9.28	5.83	3.45
	Pond Total:	**7.12**	**28.0**	**8408**	**8374**	**75.1**	**641**	**250**	**391**
Huey	0.3-0.5	42.48	16.7	779	720	5.12	16.7	0.83	15.8
	0.1-0.3	33.08	377	5245	4835	40.5	86.6	8.42	78.2
	0.05-0.1	1.55	431	2572	2139	19.7	89.9	43.0	46.9
	0.01-0.05	0.061	35.1	219.9	184.8	1.34	5.93	2.45	3.48
	Pond Total:	**77.2**	**860**	**8815**	**7878**	**66.7**	**199**	**54.7**	**144**
P70	0.56-0.96	168	50	24337	24118	284	789	67	722
	0.11-0.56	351	329	33136	32456	441	966	109.7	856
	0.06-0.11	9.232	30.8	3139	3099	29.1	83.1	4.62	78.5
	0.01-0.06	0.126	2.39	1154	1151	13.5	19.5	0.660	18.8
	Pond Total:	**528**	**413**	**61765**	**60824**	**767**	**1857**	**182**	**1675**
P70E	0.46-0.66	9.66	7.51	983	966	8.16	26.8	3.22	23.6
	0.26-0.46	3.45	2.16	410	405	3.88	10.8	1.73	9.1
	0.26-0.16	0.80	1.39	229	227	2.57	4.30	0.95	3.35
	0.16-0.06	0.13	1.43	91	90	1.20	1.78	0.50	1.28
	0.01-0.06	0.01	0.10	14.07	13.97	0.13	0.24	0.02	0.22
	Pond Total:	**14.0**	**12.6**	**1728**	**1701**	**15.9**	**44.0**	**6.42**	**37.5**

The lack of correlation between conductivity and nutrient concentrations across all ponds despite the good correlation in individual ponds reflects the variability of both major ions and nutrient concentrations in the overall composition of the pond.

Table 6.6 Total concentration of nutrients in stratified ponds layers and total pond composition of meltwater ponds sampled January 2007.

Pond	Height above sediment	NO_3-N	NH_4-N	TDN	DON	DOC	TDP	DRP	DOP
	cm	mg	mg	mg	mg	g	mg	mg	mg
Upper	0.48-0.68	102	74.6	3629	3452	26.7	294	105	189
	0.18-0.48	0.8	103	1772	1668	98.2	924	472	452
	0.03-0.18	0.8	10.3	1143	1132	11.2	124	65.3	59.0
	Pond Total:	**104**	**188**	**6545**	**6253**	**136**	**1343**	**643**	**700**
Huey	**Pond Total:**	**47.7**	**70.6**	**2412**	**2294**	**26.2**	**56.4**	**~**	**56.4**
P70	0.93-1.03	~	64.3	23319	23255	313	873	158	715
	0.53-0.93	~	320	35749	35429	528	1393	277	1116
	0.03-0.53	~	234	31550	31316	429	1171	196	976
	Pond Total:	**~**	**618**	**90618**	**90000**	**1271**	**3437**	**631**	**2807**
P70E	0.61-0.81	11.5	2.1	1128	1115	12.9	26.0	~	26.0
	0.03-0.61	2.4	72.1	6243	6169	66.1	116	~	116
	Pond Total:	**14.0**	**74.1**	**7371**	**7283**	**79.0**	**142**	**~**	**142**

As with major ions in Chapter 4, the bulk nutrient composition of each meltwater pond can be determined (see calculation methodology in Section 2.4.1). The total nutrient composition of Bratina Island meltwater ponds are given in Table 6.5 and Table 6.6 for 2005 and 2007 respectively. This calculation of bulk nutrient composition is useful in that it allows the total amount of nutrients in each pond to be compared directly without accounting for variation in pond size. Although in many cases the highest and lowest concentrations of nutrients do reflect the total volume of the pond, this is not always the case, particularly in regard to concentrations of each of the N species.

Unlike the trend seen for bulk major ion concentrations, where the pond with the greatest volume corresponded to the greatest bulk concentration of ions, nutrient concentrations did not always reflect pond volume. For example in 2005, the total DIN (the combined total of NO_3 and NH_4) in the ponds ranged from 26.6 mg in P70E Pond to 937 mg in Huey Pond, a surprising result given that Huey Pond was the smallest pond included in this study. In 2007, DIN ranged from 81.1 mg in P70E Pond to 618 mg in P70 Pond. Huey Pond, that had had such a high concentration of DIN in 2005 (937 mg) had decreased to 118 mg in 2007. This indicates that factors other than pond size and volume are influencing the concentration and availability of nutrients (although results for individual layers strongly reflect the decreasing volume of water towards the base of each pond and in the brine layer in particular). Considering the proximity of the ponds to each

other (i.e. within 200m) this cannot be explained by different regional effects, therefore it is likely that variation in the biological environment may be responsible.

In 2005, DIN in Upper Pond and Huey Pond were dominated by NH_4 rather that NO_3 while concentrations of NO_3 slightly exceeded that of NH_4 in P70 Pond and P70E Pond. In 2007 all ponds were dominated by NH_4 despite well oxygenated conditions which would be expected to favour the NO_3 species. The relatively low NO_3 may reflect the preferential uptake of this species by biological communities for growth, or the lack of NO_3 production in the ponds. Dissolved organic nitrogen made up the majority of TDN in the ponds (between 89 % and >99 %). Dissolved reactive phosphorus made up between 9 % and 37 % of the TDP in the ponds.

Bulk concentrations of DOC were higher in 2007 (26.2 g in Huey Pond and 1271 g in P70 Pond) when the ponds had been fully melted for some time compared to 2005 bulk concentrations immediately post melting (15.9 g in P70E Pond to 767 g in P70 Pond). Dissolved reactive phosphorus made up between 0 % and 48 % of the TDP in the ponds, with the highest proportion seen in Upper Pond.

6.5 Discussion 2: Biotic Processes and Ion Concentrations

The following discussion looks at the biological processes that can effect nutrient concentrations in the meltwater pond environment. Note that these reactions will only occur if thermodynamically favoured, with biota facilitating or acting as the catalyst for the reaction in order to use the energy released.

6.5.1 Biotic processes effecting nitrate concentrations

Autotrophic uptake by algal mat communities is an important process controlling NO_3 concentrations in streams (McKnight *et al.* 2004). However, it was found that concentrations of NH_4 (and all major ions) did not vary between Antarctic streams with differing abundances of algal mat indicating that these were not significantly influenced by biological processes (McKnight *et al.* 2004). Weathering and dissolution of aerosols from the hyporheic zone is an important source of nutrients to Antarctic streams in the MDV's (McKnight *et al.* 2004); this is also a potential source of nutrients to meltwater ponds that are situated on similar porous sediments. Unlike the autotrophic NO_3 uptake in the main stream channel, NO_3 uptake in the hyporheic zone is attributed to other microbial processes.

Nitrogen dynamics in MIS meltwater ponds most likely begins with an early influx of nitrogen as snowfall accumulated during winter within each pond catchment melts and enters the pond to be taken up by benthic mats and phytoplankton communities. As the growing season continues, the

role of nutrient recycling becomes increasingly important particularly in regards to NH_4. Nitrogen fixation has the potential to be an important source of N in all ponds during the summer period when irradiance levels are high. As in tidal lagoon ponds (Downes *et al.* 2000), nitrification and denitrification also occur but appear to be the least important transformation pathways in the ponds. In the basal waters of stratified ponds, changes in N concentration can be indicative of inorganic N uptake by benthic communities (Downes *et al.* 2000). Later in the summer growing season, recycling of NH_4 between cyanobacterial mats, sediment and the water column is an important process, particularly evident in intermediate and basal pond layers adjacent to the mat communities (Downes *et al.* 2000).

Dissolved oxygen and pH has been shown to be high in the upper layers of the mat profile and then decrease through the lower mat layers and into the sediment resulting in anoxic and less alkali conditions in the sediments below that creates a sub-mat environment that is favourable to N transformations (Hawes *et al.* 1993; Downes *et al.* 2000; Howard-Williams & Hawes 2007). It has been reported that NH_4 concentrations are high in interstitial mat pore waters (Hawes *et al.* 1993) and in the sub-mat sediments (Mountfort *et al.* 1999) compared to overlying meltwaters supporting this concept. Nitrate concentrations in the pond sediments are low, thus limiting the potential for denitrification despite otherwise suitable conditions (such as deoxygenated conditions and an abundance of C substrate available) (Howard-Williams *et al.* 1989; Hawes *et al.* 1993; Mountfort *et al.* 1999). Oxygen depletion in the sub-mat environment is indicative of heterotrophic activity that may recycle nutrients from organic material, potentially acting as a significant N source to the benthic community (Hawes *et al.* 1993). For the majority of time these sub-mat environments remain isolated from the overlying pond environment but in some instances rupture of cyanobacterial mat (perhaps due to gas build up or turbulence) has resulted in the rapid release of NH_4 to the water column (Hawes *et al.* 1993).

Measurements of *in situ* denitrification indicate that this is an insignificant process compared to the total uptake of NO_3 in permanently submerged mat communities; N fixation was measured *in situ* as 6.6 µg N m^{-2} h^{-1} (Downes *et al.* 2000) and was estimated as 3 - 6 mg N fixed m^{-2} $year^{-1}$ (Hawes *et al.* 1993). Since then, N-fixation has been revisited and found that average values were similar to those found in some temperature ecosystems (Quesada & Fernández-Valiente 2000).

There is a high retention of DON in the pond waters, reflecting the fact that it is relatively refractory and accumulates over time as with other major ions (Howard-Williams *et al.* 1989; Hawes *et al.* 2008), however, little is known about the sources and sinks of DON. Dissolved

organic nitrogen accumulation has been attributed to microbial activity in some of Antarctica's inland waters (e.g. Matsumoto *et al.* 1992; Downes 1986) but not others. Freeze concentration is another possible cause of DON accumulation in which case a correlation between DON and Cl would be expected (Vincent & Howard-Williams 1994). A correlation was made between salinity of the water column and DON in isolated ponds suggesting that DON accumulated like major ions over time (Vincent & Howard-Williams 1994). The ratio of DON to Cl (Figure 6.11) indicates that this is likely in some ponds e.g. P70 and P70E Pond, but not in others e.g. Eggtimer Pond which shows non-conservative behaviour with depth.

It was suggested by (Vincent & Howard-Williams 1994) that physico-chemical processes rather than biological processes were the cause of the high nitrate concentrations in meltwater ponds in the Darwin Glacier region. In this area, a strong positive relationship between conductivity and NO_3 indicated that enrichment was due to concentration mechanisms such as freezing and evaporation (Vincent & Howard-Williams 1994); however this was not seen in the MIS ponds in this study. The relatively low NO_3 concentrations in the basal layer soon after melting reflect the transformation of NO_3 to NH_4 in the anoxic winter brine environment. Cyanobacterial mat communities improve N availability by assimilating N_2 from the atmosphere which may be ultimately converted to nitrogenous compounds (e.g. NO_3-N) that can be directly used by other organisms (Quesada & Fernández-Valiente 2000). The diurnal variation in N-fixation in Antarctic meltwater ponds is significant, despite 24 hour light, especially in ponds containing the free-living cyanobacterial Nostoc, with maximum fixation rates occurring shortly after mid-day (Smith 1985). Nitrogen fixation is an energy consuming process so cyanobacteria usually stop when DIN (NH_4 or NO_3) becomes readily available or when irradiance is low (Kalff 2002).

By measuring the acetylene reducing activity (ARA) of cyanobacterial mats *in situ* is to determine levels of N_2-fixation, it was found that N_2-fixation is a common process in Antarctic mat communities regardless of the pond chemical characteristics or irradiance level (Quesada & Fernández-Valiente 2000). The ARA results suggest an average rate of N_2-fixation of 12.75 mg N m^{-2} day^{-1}, indicating that >1 g N m^{-2} may be input into the pond systems given 85 days of full light per year (Quesada & Fernández-Valiente 2000). Therefore N_2-fixation is likely to be one of the most important inputs of N to the pond ecosystems, particularly compared to N from precipitation which was estimated as just 36 mg N m^{-2} $year^{-1}$ in the Vestfold Hills (Davy 1986) and likely to be similar in the MIS region.

6.5.2 Biotic Processes effecting Phosphorus concentrations

Unlike N, P cannot be biologically fixed and must come from weathering and or atmospheric deposition (Hawes *et al.* 2008). Geochemical processes can exert strong effects on PO_4 availability, for example aerobic sediments have a strong capacity to bind PO_4 (Whalen & Cornwell 1985).

A study of soluble reactive P (SRP) behaviour in Antarctic streams found that concentrations were lower in the presence of abundant algal mats compared to when mats were absent, although concentrations of SRP were low - less than 1.57 µM. The hyporheic zone was recognised as an important source of SRP to the main stream channel (McKnight *et al.* 2004), most likely sourced through the weathering of apatite (Green *et al.* 1998; Gooseff *et al.* 2002). All PO_4 uptakes were found to be controlled by biotic processes occurring within the main stream channel (McKnight *et al.* 2004). Although this study looked at Antarctic streams not meltwater ponds, the similar nature of the cyanobacterial mat communities in these two environments suggests that biological processes are also likely to be similar.

The very low ratios of dissolved inorganic N:P in meltwater ponds on the MIS near Bratina Island are characteristic of the area (Howard-Williams *et al.* 1990) and are much lower than concentrations found elsewhere in Southern Victoria Land (Vincent & Howard-Williams 1994). Both landscape age and biotic processes can have an influence on N:P ratios with young surfaces yielding higher P concentrations and an abundance of algal mat results in lower N concentrations (Barrett *et al.* 2007). Low concentrations of DIN and high concentrations of DRP lead to very low DIN:DRP ratios, often less than 3:1 (Howard-Williams *et al.* 1989), which would theoretically promote the N_2-fixation process in N-limited environments (Smith 1985). Nitrogen fixing species have a greater competitive advantage where nitrogen concentrations are relatively low, such as those recorded in stratified tidal ponds (<1) near Bratina Island and in Pyramid trough meltwater ponds where N:P ratios are <10:1 (Vincent & Howard-Williams 1994).

Dissolved Inorganic Nitrogen: Dissolved Reactive Phosphorus Ratio

The ratio of DIN:DRP in the ponds included in this study are given in Table 6.7. Ratios of DIN:DRP for ponds for which DRP was not detected (<1 µg L^{-1}) could not be calculated including P70E Pond, VXE6 Pond and Huey Pond, and the 3 basal water layers in Eggtimer Pond.

In general these DIN:DRP ratios are very low with all except Huey Pond well below 10:1. In 2005, Upper Pond shows particularly low ratios reflecting the very high DRP concentrations measured in this pond (to a maximum concentration of 2400 µg L^{-1}). Huey Pond is the exception

with very high DIN relative to DRP with ratios up to 71:1 reflecting the very high concentrations of NO_3 (up to 8100 mg L^{-1}) measured in the pond. In 2007, Upper pond continued to have very low ratios as did P70 Pond. Based on these ratios N_2-fixation would appear to be a particularly important process in these ponds, however growth in not limited in Bratina Island ponds due to internal recycling of N (Hawes *et al.* 1993).

Table 6.7 Ratios of DIN:DRP in meltwater ponds sampled in 2005 and 2007

Pond 2005	haSed cm	DIN:DRP weight	Pond 2007	haSed cm	DIN:DRP weight
Upper	42	0.2	Upper	48	1.7
	27	0.1		18	0.2
	17	0.1		3	0.2
	7	0.1	P70	93	0.4
	1	0.2		53	1.2
Huey	30	71.0		3	1.2
	10	48.6	Orange	78	9.4
	5	10.1		8	2.0
	1	14.3		3	3.3
P70	46	3.3	Eggtimer	104	7.1
	11	6.2			
	6	8.7			
	1	3.8			
P70E	46	5.3			
	26	3.3			
	16	2.3			
	6	3.1			
	1	4.6			

6.5.3 Biotic Processes effecting Bicarbonate concentrations

Bicarbonate (or DIC) is a major ion in MIS meltwater ponds and in meltwater ponds in other areas (e.g. Victoria Land meltwater ponds) and may be influenced by biological activity. Bicarbonate is also significant due to the role it plays in determining pH. High pH in meltwater ponds over summer is the result of CO_2 and HCO_3 depletion during photosynthesis (Hawes *et al.* 1993; Hawes *et al.* 1997; Wait *et al.* 2006). As temperatures fall with the onset of winter freezing, the meltwater ponds develop a thin ice cover but photosynthesis continues while there is sufficient light, depleting concentrations of CO_2 within the pond and releasing O_2 (Schmidt *et al.* 1991). Evidence of significant DO concentrations persisting in MIS ponds until early April 2008, despite a thick ice cover, was presented in Chapter 4.4.2, and potentially influenced HCO_3 concentrations

in the residual fluid during that period. As productivity decreases with reducing light conditions, heterotrophic pathways begin to dominate pond metabolism causing the depletion of oxygen, lower pH and an increase in DIC. This has implications for HCO_3 as concentrations may increase during winter freezing.

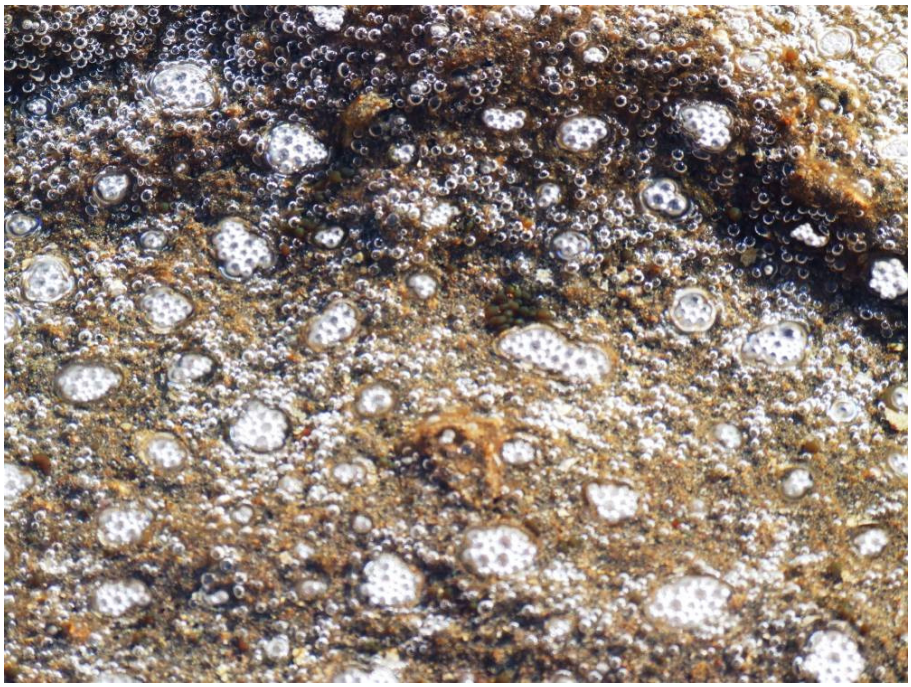

Figure 6.16 Gas bubbles, most likely the O_2 released during photosynthesis, on the surface of submerged cyanobacterial mat (January 2007).

Dissolved inorganic carbon concentrations have been shown to vary between meltwater ponds, in the MIS region but were generally low ranging from 4.5 to 89 mg L^{-1} in near edge samples collected prior to this study, with maximum concentrations occurring in ponds with higher conductivities (Hawes *et al.* 1993). The high pH measured in the ponds implies little free CO_2, with DIC predominately occurring as HCO_3 or CO_3 (Hawes *et al.* 1993). As a result of the high pH, it would appear that water column photosynthesis was carbon-limited, however lower pH and higher DIC measured in the sediments below the mats may allow higher concentrations of free CO_2 to be available to the benthic community (Hawes *et al.* 1993). In this study, DIC (measured as HCO_3) concentrations were considerably higher (ranging from 61.3 mg kg^{-1} to 5780 mg kg^{-1}) reflecting the presence of stratification and the sampling of high conductivity brines at the base of the ponds. High concentrations of O_2 released during photosynthesis forms numerous gas bubbles on the surface of cyanobacterial mat in some ponds (Figure 6.16).

Dissolved organic carbon concentrations determine the amount of C that is available for bacterial respiration (Tackacs *et al.* 2001). In the MIS ponds in this study, concentrations of DOC were

high, ranging from 7.6 mg L-1 to 640 mg L^{-1}. In comparison, maximum DOC concentrations in Antarctic lakes from the MDV's and Vestfold Hills were all less than 0.3 mg L^{-1} (McKnight *et al.* 1993; Laybourn-Parry *et al.* 2002) and the DOC in the ice cover of Lake Bonney was approximately less than or equal to 1 mg L^{-1} (Priscu *et al.* 1998). Of the DOC in Antarctic lakes only about 20 % is low molecular weight fulvic acid that is easily utilised by bacteria (McKnight *et al.* 1991; McKnight *et al.* 1993). In Antarctic lakes, DOC transformations during winter allow for the efficient recycling of photosynthetically produced organic carbon (Priscu *et al.* 1999), and create nutrient conditions suitable for phytoplankton growth in the following summer (Laybourne-Parry *et al.* 1995).

As CH_4 production in pond sediments is near equilibrium with CH_4 oxidation, and because concentrations are very low at the sediment-water interface (Mountfort *et al.* 1999), CH_4 it is not expected to have a measurable influence on the concentration of HCO_3 in the water column.

6.5.4 Biotic processes affecting redox & sulfate concentrations

Sulfate is a major component in meltwater ponds and in some cases is the dominant anion. It is an important ion for mineral precipitation with the commonly observed mirabilite being a sulfate mineral (see Chapter 4). Sulfide, the reduced species of S, can be strongly influenced by biological activity, specifically S reducing bacteria which produce H_2S and sulfur oxidising bacteria which oxidise H_2S to form SO_4. Concentrations of H_2S, when present, were significantly lower than those of SO_4 in MIS meltwater ponds making its presence or absence insignificant when modelling major chemical processes and mineral precipitation. However, S species are important in that they can be used to assess the redox potential of a meltwater pond.

Table 6.8 Modelled redox (Eh and pe) results compared to measured Eh results for selected meltwater ponds, calculated for the given water temperatures.

Pond	Height above sediment	O(-2)/O(0)		S(-2)/S(+6)		Field Measurements (*pe calculated from Eh)		
	(cm)	pe	Eh (mV)	pe	Eh (mV)	Eh (mV)	pe*	temp °C
Eggtimer	104	13.1	725			303	5.48	5.4
	24	13	722	-5.33	-297	330	5.92	7.7
	3	14	779	-4.17	-232	345	6.20	7.3
VXE6	62	13.1	725			295	5.35	4.8
	3	11.9	660	-6.4	-354	274	4.95	5.8
Upper	48	12.2	669			319	5.79	4.4
	18	12.2	681	-5.84	-326	347	6.21	8.3
	3	12.2	687	-5.74	-324	361	6.39	11.5

Hydrogen sulfide was present in the basal samples in Upper Pond and Huey Pond in 2005, the two ponds with low oxygen concentrations having only just lost their ice plug when sampled. Eggtimer, VXE6, Orange and Upper Ponds in 2007, despite oxygen saturation, had low but detectable levels of H_2S in the basal samples. This suggests, as discussed in Section 3.4.6, that biological activity is responsible for continued reduction and or release from cyanobacterial mat communities or the sediment beneath them. H_2S was present at significantly lower concentrations (up to 4 orders of magnitude lower) than SO_4 and is unlikely to play a measurable role in sulfate dynamics.

In natural aquatic environments such as Antarctic meltwater ponds, redox reactions may not have reached equilibrium conditions although this is assumed when redox values are presented (Kalff 2002). In the meltwater ponds in this study, *in situ* field measurements of Eh (Table 6.4) indicate a discrepancy between dissolved oxygen concentrations and redox values, highlighting the need for caution when interpreting and drawing conclusions from the redox results. The geochemical model PHREEQC is designed to simulate chemical reactions in low temperature aqueous solutions and is a useful tool for understanding speciation and calculating saturation indices and the distribution of aqueous species in an environment. A description of this model can be found in Chapter 2.4.1. In this case PHREEQC was used to determine the equilibrium redox conditions within the meltwater ponds based on the redox couples S(-2)/S(+6) and O(-2)/O(0); the modelled results and field measurements for Eh (and pe) of selected ponds are as shown in Table.6.8.

The Eh measured in the field ranged from 274 mV to 361 mV indicating moderately oxidising conditions. In general, aerobic environments have a redox potential >350 mV (Kalff 2002) of which only the base of Upper Pond falls into this category, despite significant concentrations of dissolved oxygen (see Table 4.3). This is a much lower oxidation potential that calculated for the O(-2)/O(0) pair which the model calculated would be between 660 mV and 779 mV reflecting a strongly oxidising environment. Conversely, field measurements of Eh are much higher than that calculated for the S(-2)/S(+6) pair which the model calculated to be between -232 mV and -354 mV that would indicate a strongly reducing environment. In effect, the field measurements of Eh reflect the fact that Eh meters take a composite measure of the redox conditions, which takes into account a whole series of factors, but does not reflect the systems capacity for specific redox reactions. This highlights one of the advantages of using geochemical modelling to investigate redox reactions as redox values are given for each redox pair rather than giving a single composite measure as is taken in the field.

The presence of any H_2S is inconsistent with the presence of dissolved oxygen as DO is a strong oxidant. In the oxygenation of organic matter, it is generally the oxidant that yield the greatest free energy change per mole of organic matter that will be used first by microbes, commencing with dissolved oxygen which will be used as a terminal electron acceptor by aerobic heterotrophic micro-organisms (Kalff 2002). This suggests that a reaction or process is taking place that is making the ponds relatively more reduced that would be expected based on DO concentrations alone.

It must be noted that the S(-2)/S(+6) redox pair was only able to be calculated when there was a measurable concentration of H_2S, the presence of which is an anomaly in itself (as discussed in Section 3.4.6). The apparent discrepancy between the S(-2)/S(+6) and O(-2)/O(0) redox couples supports the idea that ongoing biological processes are controlling the concentration and speciation of sulfide and oxygen throughout the summer period and that the pond composition is unable to reach equilibrium. Redox conditions favourable to SO_4 reduction occur in the sub-mat environment (Mountfort *et al.* 1999), where SO_4 reduction dominates over NO_3 reduction and methanogenesis (Howard-Williams & Hawes 2007), possible acting as a source of H_2S to the basal water column through the entire summer growth period. Sulfate (S+6) is reduced during microbial oxidation (respiration) of organic matter producing gaseous S^{2-} or bisulfide ion (HS-). Inorganic S is the single most important ionic determinant of the solubility of iron and many trace metals as reduced sulfide combines with Fe and trace metals to form almost insoluble precipitates under anoxic conditions (Kalff 2002).

6.6 Conclusions

The concentrations of nutrients in Bratina Island meltwater ponds are significantly lower than the concentration of major ions. Like major ion concentrations, stratification is common with nutrient concentrations increasing with depth and increasing conductivity in individual meltwater ponds, with the exception of NO_3. However, there is no clear correlation between nutrient concentrations and conductivity (or major ion concentrations) across all the meltwater ponds in this study, instead the relationship between nutrient concentrations and conductivity is specific to each pond. Nutrient concentrations do not appear to be influenced by the physical properties of the water body, such as water temperature, pH or the concentration of DO. This indicates that nutrient concentrations and their distribution within the water column are primarily controlled by the physical processes that influence major ion concentrations, such as freeze-thaw, salt exclusion and the development of stratification.

The presence of persistent stratification in some meltwater ponds allows sub-environments within the pond to be defined. Within these sub-environments, biological processes may play a more significant role as the transformation products are trapped and may accumulate within a relatively small section of the pond (i.e. the basal brine). This was particularly apparent for NO_3 which was relatively depleted at the base of the ponds most likely due to biological uptake and the lack of NO_3 production in this zone. However, for the purposes of calculating the bulk pond composition of a pond in order to predict winter conditions this would be accounted for.

Redox reactions are closely tied to the cycling of nutrients within meltwater ponds as many reactions are biologically catalysed, mediated or have implications for biological communities. The main outcome of this research in this area is that field measurements of Eh need to be treated with caution as equilibrium conditions are unlikely to occur in the meltwater pond environment. This is evidenced by measurable H_2S in the presence of O_2. Geochemical modelling has the potential to offer more detailed insights into the specific redox couples that may be influencing the field Eh measurements, however the potential biological influence remains difficult to account for.

The potential for biological processes to have a significant effect on major ion concentrations is limited due to the low concentrations of nutrients compared to those of major ions. Therefore, the precipitation and dissolution of minerals remains more likely to influence major ion concentrations than biological processes. For this reason, nutrient concentrations and the biological component of meltwater ponds can be largely ignored when using geochemical modelling tools such as FREZCHEM.

CHAPTER 7

RESEARCH OUTCOMES & CONTRIBUTIONS

Figure 7. Only in Antarctica… Ice-creams for movie night at Scott Base waiting outside in the "freezer" until intermission (January 2007).

This chapter is a synthesis of the key ideas that have been put forward in this thesis and of the conclusions made in Chapters 3, 4 5 and 6, addressing the original aims and objectives of this research. This chapter summarises the contribution that this research has made and highlights several areas that would benefit from further investigation.

7.1 Summary of this Thesis

This PhD research fully characterises the chemical extremes in Antarctic meltwater ponds over a seasonal cycle and links seasonal variations in chemistry to physical and biological processes operating within the ponds at different stages of freeze and thaw in order to better understand and predict the geochemistry of meltwater ponds during winter.

In Chapter 3, the seasonal variation that occurs in meltwater pond temperature was characterised. A high resolution record of changes in pond temperature with depth was collected alongside field observations of meltwater ponds over different seasons. A new conceptual model of freeze-thaw was developed with freezing from the top of the pond down and melting from both the bottom up and sides inwards. This conceptual model explains the physical processes that caused the unexpected temperature gradients recorded during the freezing, winter and thaw phases, and control the chemical structure of the meltwater ponds. In particular clear linkages were made between the presence of an ice plug and the geochemistry of basal brines which improves our understanding of winter processes and better enables winter brine prediction.

In Chapter 4, spatial and temporal chemical variations in meltwater ponds at different stages of freeze-thaw were investigated by comprehensive sampling of meltwater ponds at different time periods, including the late thaw phase, the summer melt phase and the freezing phase. For the first time, brine formation and development that takes place beneath the surface ice that forms during the downward progression of the freezing front was measured in 4 Bratina Island meltwater ponds which provides a basis for comparison with predicted winter brine chemistry.

In Chapter 5, validation of the geochemical model FREZCHEM62 for application in Antarctic meltwater ponds was achieved through direct comparison with observed basal brine and salt precipitate compositions. The unique samples of basal brines collected from meltwater ponds repeatedly during freezing in 2008 were directly compared to model outputs for the equivalent degree of freezing with similar predicted and observed chemistry in 3 out of 4 cases. The identification of several limitations when applying FREZCHEM62 to the meltwater pond environment, such as relying on accurate calculations of bulk pond chemistry and the potential for over prediction of carbonate mineral precipitation, combined with improved model validation enables FREZCHEM62 to be used in this environment with greater confidence in the future.

In Chapter 6, the relationship between inorganic and organic nitrogen, phosphorus, carbon and sulfate in meltwater ponds was investigated. For the first time stratification of nitrogen, phosphorus, carbon and sulfate with depth was identified in meltwater ponds and linked to the

physical and chemical factors (such as the isolation of brine beneath an ice plug during melting) that influence their distribution in the water column. Chemical reactions involving a major ion component with potential biological interaction were identified and discussed, however, when considered in the context of predicting winter brine chemistry were deemed insignificant primarily due to their low concentrations relative to major ions.

7.2 Outcomes & Contributions of this Research

This research has produced several tangible outcomes in the context of understanding the chemical extremes in Antarctic meltwater ponds over a seasonal cycle.

7.2.1 Outcome 1

Thermal gradients in meltwater ponds during freeze and thaw are determined by air temperature and the latent heat of fusion, which control the downward progression of the freezing front and heterogeneous melting during thaw. The residual 'ice plug' at the base of the pond preserves geochemical stratification into summer by isolating the basal brine. Implications for winter brine prediction are that ponds may be stratified as freezing commences, warm temperatures at the base of the pond during freeze-thaw mean brines can remain liquid for longer and any freeze concentration of DO is lost during freezing with basal brines remaining anoxic until late thaw.

A high resolution record of temperature at different depths in a Skua Pond during freezing, winter, and summer thaw highlighted the significant variation in temperature that occurs throughout a seasonal cycle. Four distinct phases were identified – summer, winter, freeze and thaw with temperatures as high as 10.3˚C and as low as -41.8˚C recorded in Skua Pond, as well as significant temperature gradients (up to 35˚C as a single time point). The downward progression of the freezing front was found to be the driving force behind salt exclusion, brine evolution, salt precipitation and the nature of the environmental conditions tolerated by microbiological communities living within these ponds during winter. It was also found that the release of latent heat of fusion strongly affected thermal gradients within meltwater ponds during both freeze and thaw, particularly at the base of the pond where temperatures stayed significantly warmer than expected during freezing.

A major outcome from this research is a much improved understanding of the physical process of freeze-thaw that differs significantly, particularly during thaw, from the "Top Down, Bottom Up" conceptual model. Instead, Bratina Island meltwater ponds freeze from the top down, potentially leaving a highly saline residual water phase at the base of the pond throughout winter, and then

melt from the base up and the sides inwards leaving a 'wine glass' shaped ice column connected to the base of the pond by an ice-plug.

The identification of ice plugs, a layer of ice trapping basal brine at the bottom of the water column, is a significant feature of the melting process and is central to understanding the transition from the winter state of the ponds to the summer state. The presence of an ice plug supports the preservation of chemical stratification into the summer melt period, acts as a barrier to chemical processes and lengthens the duration of highly saline anoxic water conditions at the base of the pond during summer with significant implications for microbial communities and the precipitation of certain minerals. Anoxic conditions also allow significant H_2S concentrations to persist well into the summer months influencing trace metal concentrations and making environmental conditions less favourable for biological production.

7.2.2 Outcome 2

The geochemistry of meltwater ponds is catchment specific with good correlation between parameters within an individual pond however there is no clear relationship between different geochemical parameters consistent to all meltwater ponds in the Bratina Island region. The basal brines that develop during freezing are nearer in composition to brines preserved during summer than those present immediately post melting, with implications for winter brine prediction. The overturn of summer stratification during freezing means that brine evolution can be based on the bulk summer chemistry of both stratified and non stratified ponds.

Regional climate and the annual cycle of freeze-thaw is the primary factor influencing the vertical distribution of major ions in meltwater ponds. The four distinct phases that occur in meltwater ponds during the annual cycle of freeze-thaw have a significant effect on the geochemical characteristics of the ponds at different times during the year. The development of stratification during the freezing phase is well preserved until the end of the thaw phase when the geochemical effect of the ice plug on the basal brine is just visible. This period shows a rapid shift from anoxic conditions to oxic conditions in the basal brine.

During the summer phase, major ions showed distinct vertical profiles consisting of an upper mixed layer and high density saline brine (≤74 mS cm^{-1}) with conductivity gradients as high as 69.2 mS cm^{-1}. Bratina Island ponds were dominated by NaCl with the chemical composition of ponds remaining similar between sampling years despite concentration changes. Deviation from the composition of the overlying water column in some basal brines indicate that processes other

than concentration, such as mineral precipitation and dissolution, were influencing brine geochemistry.

During the dynamic freezing phase the composition of the residual water during downward freezing was more similar to the basal brines persisting through the summer phase than the brines isolated beneath ice-plugs at the late stages of the thaw phase, most likely due to the depletion of ions from the water phase during winter as minerals reach saturation and precipitate out of the water column.

The mineral precipitation and dissolution that occurs as brines develop during winter and dilute during summer, particularly mirabilite, is also an important seasonal process that determines the composition of meltwater ponds throughout the year. Chemical variation between meltwater ponds reflects mineral precipitation and localised sources of salts, such as soil salts and those in the hyporheic zone, available for dissolution into the water column. Minerals identified in sediment samples from Bratina Island meltwater ponds included halite (NaCl), mirabilite ($Na_2SO_4.10H_2O$), thenardite (Na_2SO_4), magnesite ($MgCO_3$), gypsum ($CaSO_4$), sodium carbonate ($NaCO_3$) and calcite ($CaCO_3$) all of which have the potential to change the composition of meltwaters.

The factors that can cause geochemical variation in meltwater ponds include the freeze-thaw process, catchment morphology, persistence of stratification, mineral precipitation and dissolution, redox conditions and biological processes. These factors are inherently interlinked and do not occur as mutually exclusive system components meaning that the geochemical variation in a pond cannot be attributed to a single factor. However, the temperature driven freeze-thaw process and the formation of an ice plug is possibly the most significant physical factor influencing the meltwater pond geochemistry at the end of the thaw phase. The factors causing geochemical variation are also responsible for spatial and temporal variation in the Bratina Island ponds as individual processes become more or less dominant as the four seasonal phase's transition.

7.2.3 Outcome 3

FREZCHEM62 predictions of brine composition were comparable to those observed in ponds during the freezing phase and predicted mineral precipitation was consistent with minerals observed in sediment samples. Limitations still include the potential for over prediction of carbonate minerals and the need to calculate an accurate bulk pond composition from ponds that

are frequently stratified. Detailed pond bathymetry would improve the accuracy of bulk pond chemistry calculation and improve the accuracy of model outputs for winter brine prediction.

The most significant limitation to the validity of the FREZCHEM62 model, is the inherent disequilibrium that is present not only in meltwater ponds but in all natural environments. However, given the logistical constraints associated with year-round Antarctic field work, FREZCHEM62 is the most effective tool with which to estimate winter conditions in meltwater ponds, providing a reasonable approximation of many of the chemical processes occurring during meltwater ponds freezing and evaporation. If modelling limitations are acknowledged alongside FREZCHEM62 results, a valuable insight into the winter chemistry of meltwater ponds can be gained.

A comparison between actual basal brines and FREZCHEM62 modelled brine compositions for the equivalent degree of freezing yielded similar results in 3 of the 4 ponds with ratios between actual and modelled concentrations near 1. This is a significant step towards validation of the FREZCHEM62 model for the meltwater pond environment. FREZCHEM62 predictions of brine evolution in meltwater ponds during freezing indicated early precipitation of $CaMg(CO_3)_2$, $Na_2SO_4.10H_2O$ and in some instances $MgCO_3$ and $CaSO_4.2H_2O$ with $NaCl.2H_2O$, $CaCO_3$, $NaHCO_3$, KCl and $MgCl_2.12.H_2O$ precipitating as the models eutectic point was reached corresponding well to the types of salts identified in field samples. Of the 9 minerals that were predicted to precipitate, at least 5 were observed in sediment and salt samples from the area. This research is the first time that the evaporative regime of the FREZCHEM62 model has been used for Bratina Island ponds and generally minerals predicted were consistent with those found.

FREZCHEM62 outputs may be further improved by more accurate calculation of bulk pond chemistry if field measurements of pond bathymetry were available alongside geochemical information. Further validation in the form of empirical modelling and laboratory experiments of the brine formation process would also improve the reliability of FREZCHEM.

7.2.4 Outcome 4

The stratified nutrient distribution in meltwater ponds is driven by physical processes such as freeze-thaw and the development of stratification that control major ion concentrations. Low concentrations of nutrients compared to major ions mean that biological processes will have little influence on the outcome of winter brine predictions.

This research identifies that nutrient concentrations show significant changes in concentration with depth in meltwater ponds. With the exception of NO_3, nutrient concentrations tend to

increase with depth and conductivity in individual meltwater ponds. Moderate to good correlation with conductivity indicates that concentrations are primarily controlled by the same physical processes that influence major ion concentrations, such as freeze-thaw, salt exclusion and the development of stratification. However, there is no clear relationship between nutrient concentrations and conductivity (or major ion concentrations) that is consistent across all meltwater ponds sampled in this study. This indicates that catchment scale variation such as the relative productivity of the benthic mats, ultimately determines the total nutrient concentration within each pond. Additionally, nutrient concentrations do not appear to be influenced by the physical properties of the water body, such as water temperature or the presence or absence of DO.

In general, the biological influence on the concentration of major ions can be ignored when modelling pond geochemistry as nutrient concentrations were significantly lower than those of major ions. Therefore, the precipitation and dissolution of minerals is more likely to influence major ion concentrations than biological processes. Some redox reactions are closely tied to the cycling of nutrients (e.g. S(+6)/S(-2)); consequently field measurements of Eh need to be treated with caution as equilibrium conditions are unlikely to occur in the meltwater pond environment. Geochemical modelling has the potential to offer more detailed insights into the specific redox couples that may be influencing the field Eh measurements.

7.2.5 Synthesis

Although Chapters 3, 4, 5 and 6 are intended to tell a complete story on their own, each consecutive chapter builds on the one prior revealing another layer of complexity in the meltwater system. For example, in the conceptual model presented in Chapter 3, four temperature phases were identified in meltwater ponds that constitute a single seasonal cycle – the freezing phase, winter phase, thaw phase and summer phase. These four phases and the physical processes, particularly the formation of an ice plug during melting, that distinguish them provide a new context through which to consider the major ion chemistry presented in Chapter 4.

A key observation presented in Chapter 4 was the progressive formation and chemical development of brine beneath surface ice during the freezing phase. This provided essential information to enable the FREZCHEM62 model to be validated in Chapter 5. Chapter 5 also further builds on the conceptual model presented in Chapter 3 of meltwater pond freeze and thaw by using FREZCHEM62 to improve our understanding of brine evolution and mineral precipitation during freezing and evaporation. Understanding the limitations of modelling meltwater chemistry

not only improves our interpretation of model results but highlights the inherent disequilibrium and numerous variables that are present in the natural meltwater system. One of these variables is the potential influence that biology may have on the major ion chemistry of the ponds, which lead to the investigation of nutrient distribution in meltwater ponds and the discussion in Chapter 6.

7.3 Further Research

This research highlights several opportunities for further work that would add to our evolving understanding of meltwater ponds.

This thesis has established that the use of geochemical modelling is a very useful tool for the prediction of chemical conditions in meltwater ponds in winter, but recognises the potential limitations that may affect the outcome of that modelling. A useful study could involve empirical modelling of the formation of brine during freezing in a closed system from high ionic strength water. Results from this experiment could be compared to those predicted by the geochemical model FREZCHEM62 adding a second layer of validation and assessment of the ability of FREZCHEM62 to predict winter brine conditions in Antarctic meltwater ponds. Experiments could be small scale laboratory experiments where volumes of water as little as 100mls could be frozen from the top down to investigate partitioning of ions into the water and ice phase during freezing and compared to FREZCHEM62 predictions for the same solution (see similar experimental methodology in Belzile *et al.* 2002). Alternatively, or alongside this could be a more complex experiment involving larger volumes of water (e.g. 20 L) that is frozen from the surface downwards under controlled conditions to allow in situ measurement of temperature and conductivity as freezing progresses. This would allow different stages of freezing to be modelled to see at what point FREZCHEM62 differs from the laboratory based 'meltwater pond' potentially providing insight into the differences observed between predicted and observed mineral species and major ion concentrations.

While this thesis offers a comprehensive look at meltwater pond chemistry over a seasonal cycle, our current understanding of meltwater pond chemistry comes entirely from sites in the mid-Antarctic latitudes (77-78^{o}S). It would therefore be beneficial to expand on this study by including meltwater ponds at higher and lower latitudes and at varying elevations that may undergo different climatic, topographic and geological conditions, which in turn may engender different chemical processes within meltwater ponds. Further investigation into meltwater pond geochemistry at a wider variety of meltwater pond locations would also provide essential knowledge about the environmental and ecosystem functioning, and the extreme biological adaptations that may be required by organisms in inland waters of Antarctica.

Finally, this research provides a firm basis upon which to develop biological investigations that account for the chemical sub-environments that occur with depth in stratified ponds. In stratified ponds in particular, this improved understanding of pond geochemistry may help to identify factors controlling the presence or absence of specific biological communities in different sub-environments within the pond. Long-term research projects looking at the meltwater pond environment may consider adding a single basal water sample to their sampling program to sit alongside surface water samples.

7.4 Final Thoughts

The intent of this thesis was to investigate the geochemical properties of Antarctic meltwater pond environments during the climatically extreme winter season when ponds are unable to be sampled. This was achieved by developing a greater understanding of the freeze-thaw cycle and the role this plays in driving chemical changes with depth, comprehensive sampling of meltwater ponds at different stages of freeze-thaw and by assessing the relative importance of biological processes on the major ion chemistry of meltwater ponds. This research fills a significant gap in our understanding of the meltwater pond system by viewing each pond as a heterogeneous water body made up of several sub-environments including mixed surface water and concentrated basal brine layers, as well as identifying the significant seasonal variability that occurs throughout the year. This research enables winter conditions, not easily measured, to be predicted with greater confidence using the geochemical model FREZCHEM62 allowing a more complete view of the characteristics of this extreme environment to be taken. Ultimately, this research opens a door to greater understanding of biogeochemical processes that operate in meltwater ponds during winter and provides a chemical framework for the ecosystems processes operating in this unique environment.

Meltwater ponds, in their isolated Antarctic environment, are closely connected to climate, primarily being driven by regional weather events; therefore there may be wider implications of this research if meltwater ponds were found to be a good indicator of global climate change. This research, in combination with biological research, may lead to the development of ecosystem models that may be applied to more complex systems elsewhere on Earth and potentially extend to environments on other planets.

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APPENDICES

Appendix 1: All results from MIS meltwater pond samples

Table A1.1 All water quality results from MIS meltwater ponds sampled in December 2005 (haSed = height above sediment).

Pond	Depth cm	haSed cm	Temp °C	EC mS cm^{-1}	pH pH units	DO mg L^{-1}	DO* mg L^{-1}	Na mg kg^{-1}	K mg kg^{-1}	Mg mg kg^{-1}	Ca mg kg^{-1}	Cl mg kg^{-1}	SO_4 mg kg^{-1}	HCO_3 mg kg^{-1}	H_2S mg kg^{-1}	NO_3-N mg m^{-3}	NH_4-N mg m^{-3}	TDN mg m^{-3}	DON mg m^{-3}	DOC mg kg^{-1}	TDP mg m^{-3}	DRP mg m^{-3}	DOP mg m^{-3}
Upper	20	42	4.9	7.5	9.88		13.9	1720	41.0	50.1	27.0	1727	1060	308	0.049	4	9	4010	3997	32.2	232	60	172
	35	27	5.1	13.6	9.94		7.6	3320	71.0	84.8	24.0	3027	2475	576	0	3	31	6090	6056	61.2	589	264	325
	45	17	5.1	16.5	9.9		4.7	4050	88.0	110	23.0	3769	3305	686	0	5	28	5780	5747	73.8	680	343	337
	55	7	4.7	26.6	9.71		1.3	7810	195	221	18.0	9159	4657	1468	0	21	48	20300	20231	157	1850	1090	760
	61	1	3.8	39.3	9.65		1	11700	290	333	17.0	13207	6574	2332	0.200	23	391	34000	33586	329	3820	2400	1420
Huey	20	30	9.4	4.17	9.58		12.9	680	25.0	89.3	38.0	1114	192	107	0	102	40	1870	1728	12.3	40	2	38
	40	10	9.4	16.45	9.39		6.2	3480	130	420	53.0	5584	722	289	0	55	626	8720	8039	67.4	144	14	130
	45	5	8	32.3	9.44		2.3	7310	293	1020	56.0	7718	1923	689	10.5	20	5570	33200	27610	254	1160	555	605
	49	1	6.9	41.8	9.37		1.27	10200	393	1420	62.0	9295	2462	796	14.8	14	8100	50800	42686	309	1370	566	804
P70	40	46	7.5	4.78	9.32	12.3	No Instrument Profile	856	34.0	112	34.0	1421	195	136	0	10	3	1450	1437	16.9	47	4	43
	85	11	7.5	5.02	9.38	12.3		877	35.0	113	36.0	1509	203	143	0	16	15	1510	1479	20.1	44	5	39
	90	6	7.1	5.5	9.49	13.6		985	41.0	121	40.0	1641	217	158	0	6	20	2040	2014	18.9	54	3	51
	95	1	6.5	74	7.95	14.5		22700	735	2810	353	36581	6883	2318	0	4	76	36700	36620	428	620	21	599
P70E	20	46	4	6.17	8.6		12.6	844	31.0	187	149	1980	146	61.3	0	9	7	916	900	7.6	25	3	22
	40	26	3.5	7	8.81	10.9	15.8	837	32.0	185	148	1983	150	62.2	0	8	5	951	938	9.0	25	4	21
	50	16	6.5	22.54	8.8		>20	3560	123	812	609	8204	558	80.4	0	11	19	3140	3110	35.2	59	13	46
	60	6	5	34.6	8.12	14.6	16.8	7680	245	1810	1400	17616	1001	225	0	6	68	4340	4266	57.2	85	24	61
	66	1	4	55	8.2	16.7	20	12000	385	3040	2110	28616	1785	270	0	7	84	12100	12009	110	210	20	190

Table A1.2 All water quality results from MIS meltwater ponds sampled January 2007 (haSed = height above sediment).

Pond	Depth cm	haSed cm	Temp °C	EC mS cm^{-1}	pH pH units	DO mg L^{-1}	Eh mV	Na mg kg^{-1}	K mg kg^{-1}	Mg mg kg^{-1}	Ca mg kg^{-1}	Cl mg kg^{-1}	SO_4 mg kg^{-1}	HCO_3 mg kg^{-1}	H_2S mg kg^{-1}	NO_3-N mg m^{-3}	NH_4-N mg m^{-3}	TDN mg m^{-3}	DON mg m^{-3}	DOC mg kg^{-1}	TDP mg m^{-3}	DRP mg m^{-3}	DOP mg m^{-3}
Upper	20	48	4.4	4.51	10.06	12.6	319	1213	33.5	34.7	17.7	1196	861	286	0.000	91	66	3220	3063	23.7	261	93	168
	50	18	8.3	16.31	9.72	12.9	347	5893	146	168	20.0	6481	3206	1196	0.002	1	162	2780	2617	154	1450	741	709
	65	3	11.5	36.1	9.5	12.7	361	14202	321	385	0.96	13987	10006	2811	0.103	22	291	32370	32057	316	3520	1850	1670
Huey	25	28	7.7	3.68	10.08	12.2	234	921	41.2	100	39.0	1549	199	85.0	nd	40	59	2010	1911	21.8	47	<1	47
P70	10	93	6.5	3.86	9.62		247	1018	41.1	103	40.8	1666	250	121	nd	<1	5	1950	1945	26.2	73	13	60
	60	53	6.2	3.86	9.67		236	1057	40.9	108	43.2	1738	252	119	nd	<1	17	1950	1933	28.8	76	15	61
	110	3	5.9	3.93	9.69		240	991	41.9	116	43.2	1710	264	122	nd	<1	15	2020	2005	27.5	75	13	62
P70E	20	61	8.7	5.66	8.65	11.4	281	1080	41.8	210	201	2268	155	93.9	0.000	11	2	1040	1027	11.9	24	<1	24
	78	3	7.2	35.1	9.01	12.6	255	5785	230	1357	1724	13876	1240	66.3	0.000	3	88	7660	7569	81.1	142	<1	142
Orange	50	78	4.2	2.1	9.82		232	656	27.0	40	14.6	847	151	295	0.000	7	55	2130	2068	21	102	7	95
	120	8	4.5	6.28	9.68		245	2102	79.5	118	0.00	2533	439	2449	0.105	<1	135	4840	4705	93.4	406	68	338
	125	3	4.9	32.2	9.21		244	10895	451	536	0.00	12764	2438	5784	0.325	<1	601	38660	38059	640	1560	180	1380
VXE7	30	62	4.8	5.74	9.02	10.4	295	1330	50.5	195	150	1977	640	100	0.000	2	19	1800	1779	19.9	41	<1	41
	85	7	5.2	19.81	9.54		0	2527	227	953	872	4519	1509	121	0.000	2	84	8170	8085	78.8	154	<1	154
	89	3	5.8	35.2	10.19	12.0	274	7680	286	1079	907	12388	3515	94.0	0.016	4	97	4470	4369	127	210	<1	210
Eggtimer	50	104	5.4	2.5	9	11.6	303	713	25.2	75.1	30.1	1232	175	189	0.000	2	123	6620	6495	13.9	207	18	189
	130	24	7.7	19.63	8.99	11.1	330	5706	183	528	80.8	9782	1317	1165	0.057	3	239	431	189	108	346	<1	346
	140	14	8.8	40.4	8.41		338	14155	394	911	129	21870	2986	3019	0.064	7	8	935	921	193	26	<1	26
	151	3	7.3	64.1	8.03	14.1	345	23259	650	1640	189	36923	7280	5608	0.056	<1	270	24760	24490	406	455	<1	455
Son of Salt	surface		9.4	11.84	8.97			3013	27.2	19.0	129	764	6087	443	nd	13	16	1670	1640		355	166	189
Slimy	surface		11.9	26.4	10.69			8610	208	220	486	3728	16499	126	nd	2730	147	11250	8373		472	<1	472

Appendix 2: High Resolution Pond Profiling

Table A2.1 High resolution profiles of selected physical properties through the water column of meltwater ponds sampled in December 2005.

Pond/Year	Depth	Height above Sediment	Temperature	Conductivity	pH	Eh	DO
	cm	cm	°C	mS/cm	pH units	mV	mg/L
Upper 2005	5	57.5	7.4	8.02	9.95	-183	12.7
	10	52.5	7.4	8.04	9.99	-179	13.6
	15	47.5	7.4	8.04	10	-179	14.1
	20	42.5	7	8.1	10.01	-181	13.9
	25	37.5	6.7	8.17	10.06	-182	12.9
	30	32.5	6.4	12.68	10.06	-183	10.5
	35	27.5	6.2	14.84	10.04	-183	7.6
	40	22.5	5.9	16.26	10.03	-184	5.7
	45	17.5	5.5	17.86	10.01	-186	4.7
	50	12.5	5.2	20.64	9.93	-189	2.5
	55	7.5	4.9	24.67	9.84	-191	1.3
	60	2.5	4.2	35.4	9.74	-196	1.2
	61.5	1	3	48.6	9.66	-227	1
P70E 2005	5	66	7.4	6.82	8.85	-222	12.8
	10	61	7.4	6.9	8.9	-216	12.3
	15	56	7.4	6.9	8.9	-213	12.5
	20	51	7.4	6.9	8.9	-212	12.6
	25	46	7.4	6.89	8.9	-211	12.3
	30	41	7.3	6.89	8.9	-208	12.6
	35	36	7.1	6.9	8.92	-207	12.5
	40	31	7	7.52	9.13	-203	15.8
	45	26	7.5	16.85	9.2	-183	>20
	50	21	7.8	20.07	8.97	-173	>20
	55	16	8.3	24.2	8.5	-176	19.2
	60	11	8.3	31.4	8.2	-171	16.8
	65	6	8.7	41.4	8.26	-163	>20
	70	1	8.2	58.3	7.84	-172	20
P70 2005	10	87	4.7	7			
	20	77	4.63	7.1			
	30	67	4.7	7.2			
	40	57	4.71	7.2			
	50	47	4.71	7.3			
	60	37	4.71	7.3			
	70	27	4.7	7.3			
	80	17	4.71	7.3			
	90	7	9.8	7			
	95	2	47.9	6.8			
	96	1	52	6.7			
Huey 2005	5	47	7.4	4.33	9.37	-252	12.5
	10	42	7.4	4.28	9.41	-249	12.8
	15	37	7.3	4.27	9.42	-249	13.1
	20	32	7.2	4.26	9.42	-247	12.9
	25	27	7.1	4.25	9.43	-244	12.8
	30	22	6.6	4.26	9.44	-245	12.6
	35	17	6.2	4.41	9.43	-258	9.9
	40	12	6	9.43	9.36	-273	6.2

	45	7	6.2	24.26	9.29	-300	2.3
	50	2	5.5	38.8	9.43	-326	1.27
	51	1	4.6	44.4	9.13	-294	1.3
VXE6 2005	10	90	4.8	2.9			
	20	80	4.74	3.1			
	30	70	4.72	3.2			
	40	60	4.71	3.2			
	50	50	4.7	3.2			
	60	40	4.69	3.2			
	70	30	4.68	3.3			
	75	25	5.2	3.1			
	80	20	9.3	3.2			
	85	15	25.8	2.9			
	90	10	38.3	2.3			
	95	5	57.9	1			
	99	1	75	-0.3			

Table A2.2 High resolution profiles of selected physical properties through the water column of meltwater ponds sampled in January 2007.

Pond/Year	Depth	Height above Sediment	Temperature	Conductivity	pH	Eh
	cm	cm	°C	mS/cm	pH units	mV
Upper 2007	10	58	4.3	4.42	9.96	119
	20	48	4.4	4.42	9.98	120
	30	38	4.4	4.43	9.99	118
	40	28	4.5	4.44	10.01	116
	50	18	8.4	16.52	9.6	148
	60	8	11.3	32.7	9.43	160
	67	1	11.3	43.1	9.44	162
	-1	-1				-230
	-6	-6				-250
P70E 2007	10	71	8.7	5.64	8.31	81
	20	61	8.7	5.63	8.35	82
	30	51	8.7	5.63	8.36	84
	40	41	8.7	5.64	8.38	83
	50	31	8.7	5.64	8.39	84
	60	21	8.7	5.64	8.4	86
	70	11	8.7	5.64	8.5	93
	80	1	12.5	40.8	9.45	56
	81	0				
	-1	-1				-108
	-5	-5				-221
	-10	-10				-229
P70 2007	10	100	6.03	5.3		
	20	90	6.21	5.3		
	30	80	6.22	5.4		
	40	70	6.21	5.4		
	50	60	6.22	5.4		
	60	50	6.22	5.4		
	70	40	6.22	5.4		
	80	30	6.22	5.4		
	90	20	6.22	5.4		
	100	10	6.22	5.4		

	110	0	11.5	7		
Huey 2007	10	43	7.9	3.73	10.1	51
	20	33	7.8	3.69	10.08	51
	30	23	7.7	3.68	10.08	51
	40	13	7.6	3.68	10.07	51
	50	3	7.9	3.98	10.18	57
	53	0	10	6.05	9.03	
	-1	-1				-247
	-5	-5				-280
	-10	-10				-289
VXE6 2007	10	83	10.06	7.9		
	20	73	10.04	8		
	30	63	10.03	8		
	40	53	10.02	8		
	50	43	10.02	8		
	60	33	10.02	8		
	70	23	10.01	8.1		
	80	13	11.03	9.8		
	85	8	29.6	12.1		
	90	3	49.3	13.6		
	92	1	55	14		
Orange 2007	10	106	3.76	8.7		
	20	96	3.75	8.8		
	30	86	3.75	8.9		
	40	76	3.76	9		
	50	66	3.75	9		
	60	56	3.74	9.1		
	70	46	3.73	9.1		
	80	36	3.73	9.1		
	90	26	3.73	9.1		
	100	16	3.73	9.1		
	110	6	3.73	9.1		
	115	1	40.1	11.2		
Eggtimer 2007	10	146	3.78	4.9		
	20	136	3.78	5.1		
	30	126	3.84	5.3		
	40	116	3.83	5.4		
	50	106	3.85	5.4		
	60	96	3.86	5.4		
	70	86	3.88	5.4		
	80	76	3.88	5.4		
	90	66	3.89	5.4		
	100	56	3.89	5.5		
	110	46	3.89	5.4		
	120	36	3.9	5.5		
	130	26	6.25	7.7		
	135	21	28.8	8.7		
	140	16	49.8	8.8		
	145	11	62.8	8.4		
	150	6	69.6	7.8		
	155	1	71.5	7.3		

Appendix 3: Late Season Physical Data

Table A3.1 Ice thickness (in cm) measured from the pond surface downwards in selected meltwater ponds between February and April 2008. "nm" indicates that no measurement was taken on that day.

Date	Julian Day	P70	Orange	Eggtimer	Skua
02/02/08	33	0	0	0	0
06/02/08	37	1	nm	nm	nm
11/02/08	42	5	6	5	9
13/02/08	44	8	9	nm	nm
15/02/08	46	13	12	nm	nm
18/02/08	49	15	nm	nm	nm
20/02/08	51	21	22	22	20
26/02/08	57	25	28	24	25
03/03/08	63	29	29	31	30
06/03/08	66	34	34	33	nm
10/03/08	70	38	39	42	36
13/03/08	73	*43*	*37*	44	nm
17/03/08	77	50	50	51	49
20/03/08	80	57	58	59	nm
25/03/08	85	61	69	71	66
02/04/08	93	72	80	76	78
07/04/08	98	81	95	97	90

Table A3.2 The physical characteristics of Egg(timer) Pond (formerly Eggtimer Pond) with depth during progressive freezing. Measurements were taken in situ between February and April 2008. Temperature (T) is given in ˚C, dissolved oxygen (DO) is given in mg L^{-1}, and electrical conductivity (EC) is given in mS cm^{-1}.

Pond	12/02/08			16/02/08			21/02/08		26/02/2008*			3/03/08			6/03/08			10/03/08			14/03/08			17/03/08			25/03/2008**			2/04/08			7/04/08		
Depth	T	DO	EC	T	DO	EC	DO	EC	T	DO	EC	T	DO	EC	T	DO	EC	T	DO	EC	T	DO	EC	T	DO	EC	T	DO	EC	T	DO	EC	T	DO	EC
10	1.1	34	4.56																																
20	1.4	33.8	4.35	2.2	31.7	6.22	31.4	8.87	0.7		8.69																								
30	1.7	34	4.3	1.7	31.6	6.03	31.9	8.85	0.7	33.7	8.77	-0.4	29.4	9.58	0.4	24.2	10.1			12.2															
40	1.9	34.5	4.31	1.5	31.4	5.92	32.1	8.83	0.8	33.4	8.77	-0.4	29.2	9.61	0.3	25.1	10.3	-0.4	34.5	12.2	-0.4	21.7	13												
50	2.6	35.3	4.33	1.6	31.7	5.89	31.8	8.83	0.8	32.9	8.77	-0.4	28.8	9.6	0	25.5	10.3	-0.4	34.5		-0.4	21.8	13												
55	2.7	35.4	4.38																	12.2				-0.6	23.7	13.7									
60	3.2	35.7	4.44	1.7	30.9	6.01	32.2	8.79	0.8	32.9	8.77	-0.4	28.6	9.6	0	25.6	10.2	-0.4	32.4		-0.5	22.1	13	-0.6	23.9	13.7									
65	2.8	35.4	4.55	1.6	30.9	6.07		8.76	0.9		8.76				0	25.6	10.2			12.1															
70	2.3	35.2	4.68	1.5	30.5	6.08	32.1	8.79	0.8	32.4	8.76	-0.4	28.4	9.59	-0.1	25.5	10.2	-0.4	34.1		-0.5	22.1	13	-0.6	24	13.7	-0.4	19.2	18.9						
75	2	35.1	4.8	1.4	31.2	6.12		8.79	0.7		8.77	-0.4			-0.1	25.6	10.1			12.1															
80	2.2	35.5	4.99	1.4	30.8	6.23	32.3	8.8	0.7	31.4	8.79	-0.4	28.1	9.6	-0.2	25.8	10	-0.4	34.7		-0.5	22.2	13	-0.6	24.1	13.7	-0.4	19.2	19.1	-1.2	16.6	26.2			
85	3	36.2	5.13	1.4	31.1	6.33	31.8	8.76	0.7	30.7	8.79	-0.4			-0.3	25.7	10			12															
90	3.5	38	5.25	1.6	30.8	6.49	32.2	8.76	0.7	30.4	8.79	-0.4	27.8	9.62	-0.3	25.7	10	-0.4	34.6		-0.5	22.4	13	-0.6	23.5	13.7	-0.5	19.2	19.1	-1.2	16.6	26.1			
95	4	40	6.05	1.8	30.9	7.32	33.3	8.74	0.8	30.2	8.89	-0.4	27.8	9.62	-0.4	25.9	10			12.1															
100	5.5	53.2	9.5	2.7	46.7	10.8	40.4	9.09	1	31.8	10.2	-0.4	27.8	9.75	-0.6	25.8	11.1	-0.6	34.8	14	-0.5	22.5	13	-0.6	23.9	13.7	-0.6	19.4	19.1	-1.2	16.4	26.1			
105	6	64.9	18	3.3	58	16.3	54.9	13.3	1	59.4	17.1	-0.4	30.2	11.6	-0.7	25.8	13.9	-0.8	34.8	21.3	-0.5	22.5	13	-0.7	26.7	13.7	-0.6		19.1						
110	6	78.4	29.5	3.4	62.6	28.2	68.7	24.8	0.8	72.2	27.7	-0.5	48.7	21.7	-1	43.1	23.2	-1.1	34.8	29.1	-1	22.5	15.9	-1.1	27	17.7	-0.7	19.4	19.2	-1.1	16.3	26.1	-1.2	11.5	36.9
115	5.8	84.4	39.6	3.5	70.8	36.6	72	31.4	0.6	76.8	37.6	-0.6	56.9	28.6	-1.1	46.3	30.6	-1.2	44.8	37.6	-1.3	30.1	23.5	-1.4	35.8	24.1	-1.1	19.4	21.3	-1.2		26.1			
120	5.6	87.6	49.3	3.3	76.6	45.6	77.2	41.8	0.6	85.8	46.5	-0.7	63.1	37.8	-1.5	51.9	38.6	-1.5	59.8	46.8	-1.5	39.7	32.9	-1.6	39.5	33.2	-1.4	19.4	27.5	-1.3	16.2	26.2	-1.3	11.4	36.9
125	5.1	89.1	54.1	2.9	66.8	54.5	84.5	50.6	0	88.1	54.4	-1.1	63.5	46.6	-1.6	52.4	45.2	-1.8	66.2	53.1	-1.8	40.9	38	-1.9	39.3	40.4	-1.6	36.6	35.2	-1.8	20.5	35			
130								51.4	-0.4	90.9	62.6	-1.3	64.2	55.4	-1.8	52.9	52.7	-2	68.3	60.6	-2.2	42.7	50.1	-2.2	35.2	47.9	-1.9	38.3	43.3	-2	27.4	41.1	-1.5	11.4	39.7
135									-0.7	91.9	58.8				-2.2	52.1	59.8	-2.3	68.2	61.4	-2.4	43.4	54.7	-2.5	35.3	55.8	-2.2	40.8	48.8	-2.4	28.3	48.1	-1.8		41.8
137																		-2.4									-2.7		55.6						
140																					-2.6	40.2	63.8	-2.7	32.3	62		40.3		-2.7	12.4	54.2	-2.1	11.4	50
143																						34.6													
145																														-3	5.88	53.4	-2.3	2.88	53.5
150																																	-2.6	0.46	60.6

* DO was collected the following day on the 27/02/08

** DO was collected the following day on the 26/03/08

Table A3.3 The physical characteristics of Orange Pond with increasing depth during progressive freezing. Measurements were taken in situ between February and April 2008. Temperature (T) is given in ˚C, dissolved oxygen (DO) is given in mg L^{-1}, and electrical conductivity (EC) is given in mS cm^{-1}.

Pond	6/02/08			12/02/08			16/02/08			21/02/08			26/02/2008*			3/03/08			6/03/08			10/03/08			14/03/08			17/03/08			25/03/2008**			2/04/08			7/04/08		
Depth	T	DO	EC	T	DO	EC	T	DO	EC	T	DO	EC	T	DO	EC	T	DO	EC	T	DO	EC	T	DO	EC	T	DO	EC	T	DO	EC	T	DO	EC	T	DO	EC			
10	3	nm	3.8	1.8	34	1.9																																	
20	3.3	nm	3.8	1.9	34	1.8	1.4	38	4.4	3.2	40	6.4	1		6.7																							
30	3.5	nm	3.8	1.9	34	1.6	1.7	40	4.4	3.3	40	6.5	1	41	6.7	-0	34	8	0.3	34	7.6																	
40	3.4	nm	3.8	2.1	34	1.6	1.8	40	4.4	3.2	40	6.5	1.1	38	6.6	-0	33	8	0.2	34	8	0	33	9.2	-1	20	9.9											
50	3.5	nm	3.9	2.5	35	1.6	2.3	39	4.4	3.2	40	6.5	1.1	38	6.7	-0	33	8	0	34	7.9	-0	34	9.3	-1	21	9.9			0								
55		nm		2.7	35	1.6																						-1	16	9.8								
60	3.4	nm	3.9	3	35	2	2.7	40	4.4	3.2	40	6.5	1.1	38	6.7				0	33	7.9	-0	34	9.3	-1	21	9.9	-1	16	9.7								
65		nm		3.3	35	2.4	3.3	40	4.4	3.2		6.5	1.1	38	6.7	-0	33	7.9	0	33	7.9				-1		9.9											
70	3.6	nm	3.9	3.6	35	2.5	3.3	40	4.5	3.2	40	6.5	1	38	6.6	-0	33	7.9	-0	33	7.8	-0	34	9.2	-1	21	9.9	-1	17	9.6	-1	12	16					
75		nm		3.8	36	2.6	3.3	39	4.8	3.2	40	6.5	1	38	6.7	-0	33	7.9	-0	33	7.8	-0	34	9.2	-1		9.9				-1		16					
80	4.1	nm	3.9	4.3	37	2.7	3.5	40	4.8	3.2	40	6.5	1	38	6.7	-0	33	7.9	-0	33	7.8	-0	34	9.2	-1	21	9.9	-1	17	9.6	-1	11	16	-1	3.6	23		
85		nm		5.1	51	3.6	4.2	44	7.7	3.7	40	7	1.2	39	7	-0	33	7.9	-0	33	7.8	-0	34	9.2	-0		9.9	-1		9.5	-1		16					
90	6.5	nm	0.5	6.2	59	7.1	4.6	52	15	3.9	44	9.6	1.2	41	9.5	-0	33	7.9	-0	33	7.8	-0	34	9.3	-1	21	9.9	-1	17	9.5	-1	11	16	-1	3.4	23		
95		nm		6.7	63	24	5	61	25	4.3	49	16	1.3	42	17	-0	34	9.5	-0	32	9.3	-1	34	11	-1	21	9.9	-1	18	9.5	-1	11	16					
100	8.3	nm	21	7	63	34	5.1	73	34	4.4	55	35	1.3	47	26	-0	36	15	-1	40	14	-1	34	16	-1	21	11	-1	22	12	-1	10	16	-1	3.3	23	-2	1	33
105		nm		6.7	66		5	70	40	4.5	59	37	1.2	50	35	-0	41	22	-1	41	22	-1	49	24	-1	21	16	-1	23	18	-1	10	20		3.2				
107	8.4	nm	42							4.4	59	41	1.1						-1	40	25							-2	22	23	-1		26					
108														52														-2	17	21	-2		32					
110																-1	39	33			*33*	-1	51	33	-1	25	26				-2	10	34	-1	3	23	-2	0.9	34
112																						-2	48	30														
115																									-2	25	35					10		-1	2.8	23		0.8	
120																									-2	26	37					9.5		-2	2.4	23	-2	0.7	34
125																																9.5				*35*	-2	0.6	35
127																																					-2	0.6	34

* DO was collected the following day on the 27/02/08

** DO was collected the following day on the 26/03/08

Table A3.4 The physical characteristics of P70 Pond with increasing depth during progressive freezing. Measurements were taken in situ between February and April 2008. Temperature (T) is given in ˚C, dissolved oxygen (DO) is given in mg L^{-1}, and electrical conductivity (EC) is given in mS cm^{-1}.

Pond	6/02/08		12/02/08			16/02/08			18/02/08			20/02/08			22/02/08	26/02/2008*			3/03/08			6/03/08			10/03/08		14/03/08			17/03/08			25/03/2008**			2/04/08			7/04/08		
Depth	T	EC	T	DO	EC	T	DO	EC	T	DO	EC	T	DO	EC	DO	T	DO	EC	T	DO	EC	T	DO	EC	T	EC	T	DO	EC	T	DO	EC	T	DO	EC	T	DO	EC	T	DO	EC
10	3.4	5.91	0.4	35.6	5.51																																				
20	3.5	5.89	1	35.4	5.31	1.4	33.2	5.74	1	44.9	7.77	0	45.7	9.49	41.9	0.5		9.92																						
30	3.5	5.89	1.3	33.9	5.27	1.4	32.5	5.63	1.3	44.1	7.88	0	46.6	9.78	42.9	0.5	34.4	10	-0.4	29.2	11.5	0.8	22.5	12.8															
40	3.5	5.89	1.8	33.3	5.3	1.6	33.4	5.51	1.4	44.4	7.99	0.1	47	9.78	43.2	0.4	33.8	10	-0.4	30.7	11.5	0.5	24.2	12.7	-0.4	14.6	-0.1	19.7	17										
50	3.5	5.91	2.2	33	5.3	1.8	32.3	5.46	1.4	43.3	8.1	0.3	47.6	9.76	43.6	0.4	33.8	10	-0.4	30.7	11.5	0.3	24.2	12.6	-0.4	14.6	-0.2	19.9	17.1										
55				33								0.4	47.9				33.5													-0.8	20.3	18.2								
60	3.5	5.91	2.2	33.7	5.31	1.8	32.5	5.44	1.4	43	8.19	0.4	48.2	9.76	43.6	0.4	33.5	9.99	-0.4	30.9	11.5	0.2	24.4	12.5	-0.4	14.6	-0.3	20.1	17.1	-0.8	20.3	18.2								
65			2.3	34.1	5.32	1.8	32.5	5.46	1.4	42.5	8.19	0.5	48.5	9.77	43.1	0.4	33.1	9.99	-0.4	31.2	11.5	0.1	24.7	12.4	-0.4	14.7	-0.4	20.2	17				-0.9		26.7					
70	3.5	5.92	2.4	34.8	5.5	1.8	33.8	5.47	1.4	43.3	8.23	0.5	48.8	9.75	43.2	0.3	33.1	9.98	-0.4	31.2	11.5	0	25.1	12.4	-0.4	14.6	-0.4	20.2	17	-0.8	20.5	18.2	-0.9	12.9	26.7					
75			2.5	34.7	5.51	1.7	34.6	5.48	1.5	44.4	8.25	0.6	49.2	9.77	43.2	0.3	32.9	9.98	-0.4	31.7	11.5	0	25.5	12.3	-0.4	14.6	-0.4	20.1	17				-0.9		26.8					
80	3.6	5.92	2.5	35.3	5.51	1.7	34.9	5.49	1.6	43.1	8.35	0.6	49.4	9.75	43.4	0.4	32.5	9.98	-0.4	31.8	11.5	0	25.6	12.3	-0.5	14.6	-0.4	20.3	17	-0.8	20.5	18.2	-1	12.6	26.8	-1.4	5.67	34.5	-1.5		46.2
85	3.6	5.93	2.3	35.8	5.53	1.8	34	5.51	1.6	42.9	8.3	0.6	49.8	9.76	43.5	0.4	32.5	9.98	-0.4	32.5	11.5	0	25.7	12.1	-0.5	14.6	-0.4	20.4	17	-0.8	21	18.2	-1.1		26.8					
90	3.7	5.93	2.2	35.7	5.66	2	33.9	5.52	2	40.8	8.39	0.7	50.2	9.75	43.7	0.5	32.6	9.98	-0.4	32.6	11.5	0	25.8	12.1	-0.5	14.6	-0.4	20.4	16.9	-0.8	21.2	18.2	-1	12.6	26.8	-1.4	5.57	35.4	-1.5	0.46	46.1
95	4.4	5.96	2.9	37.7	5.77	2.1	37	5.52	2.4	49.2	8.69	1.1	50.7	9.75	44.0	0.6	32.6	10.2	-0.4	33	11.5	-0.1	26.1	12.1	-0.5	14.6	-0.4	20.5	16.9	-0.7	21.2	18.2	-1	12.3	26.7	-1.4		35.4	-1.5		46.1
100	5.9	5.97	4.1	51.2	7.33	3.3	48.5	5.54	3.3	70.9	10.2	1.6	53.7	9.92	44.4	0.8	46	13	-0.4	32.8	11.5	-0.1	26.4	12.1	-0.4	14.6	-0.4	20.5	16.9	-0.7	21.3	18.2	-1	12.2	26.7	-1.4	5.47	35.7	-1.5	0.35	46.3
105	6.1	6.72	4.9	81.3		3.9	54.4	6.66				2.3	67.6	11.5	60.4	0.6		14.3	-0.4	35.8	14	-0.3	26.6	12.9	-0.5	14.6	-0.5	20.5	16.9	-0.7	21.4	18	-1	11.8	26.6	-1.5	5.36	35.7	-1.5		46.4
107												2.6	161	13.8					-0.5	0	16.2									21.2									
108																						-0.4	26.5	15.7																
110																									-0.7	16.1	-0.7	20.5	17.6							-1.4	5.26	35.9	-1.5	0.35	46.4
113																												20.7												
115																												18.5					11.7		-1.4	5.16	35.6	-1.5	0.23	45.8

* DO was collected the following day on the 27/02/08

** DO was collected the following day on the 26/03/08

Table A3.5 The physical characteristics of Skua Pond with increasing depth during progressive freezing. Measurements were taken in situ between February and April 2008. Temperature (T) is given in ˚C, dissolved oxygen (DO) is given in mg L^{-1}, and electrical conductivity (EC) is given in mS cm^{-1}.

Pond	11/02/08			21/02/08			22/02/08		26/02/2008*		3/03/08			10/03/08		14/03/08			17/03/08		25/03/08		2/04/08			7/04/08		
Depth	T	DO	EC	T	DO	EC	T	DO	DO	EC	T	DO	EC	T	EC	T	DO	EC	T	DO	T	EC	T	DO	EC	T	DO	EC
10	2.4	28.7	1.05																									
20	3.2	29.8	1.07	0.6	29.2	1.68	1.3	30.1		1.56																		
30	3.4	29.2	1.08	1.8	30.3	1.61	1.7	29.4	31.2	1.56	0.3	30.5	1.68															
40	3.4	29.2	1.09	2.8	31.5	1.63	2.6	30.5	31.8	1.58	1	30.7	1.68	0.3	1.94	0	27.3	2.58										
50	3.4	29.4	1.1	2.9	31.8	1.63	2.7	31.2	33	1.58	1.4	30.7	1.68	0.5	1.95	0	26.8	2.59	2.69	25								
60	3.4	29.7	1.11	3.2	32	1.61	2.8	31.7	31.4	1.58	1.7	31	1.68	0.7	1.96	0.3	27.1	2.53	2.69	26								
70	3.4	29.9	1.14	3.5	32.3	1.6	2.9	32	32.6	1.59	2.1	32	1.67	1.1	1.96	0.4	27.6	2.5	2.69	26.6	-0.3	3.29						
75						1.6				1.6																		
80	3.6	29.9	1.15	3.8	32.4	1.59	3.1	32.3	31.8	1.61	2.2	31.9	1.65	1.2	1.97	0.6	27.4	2.51	2.69	27.4	-0.3	3.29	-0.4	27	2.46			
85						1.59				1.63																		
90	3.8	31	1.16	3.8	30.9	1.59	3.9	32.6	33	1.65	2.2	30.8	1.67	1.2	2	0.6	27.8	2.49	2.69	27.5	-0.3	3.28	-0.4	27	2.41	-0.6	22.1	4.84
95						1.59	4.1	32.7	31.9	1.66	2.3	30.6	1.67							27.9								
100	4.8	31.5	1.21	4.2	29.4	1.6	4.2	33.4	30	1.68	2.4	29.7	1.67	1.1	2.02	0.7	28	2.46	2.69	28.3	-0.2	3.28	-0.4	27	2.37	-0.6	21.9	4.81
105				4.3	30.1	1.65	4.4	32.7	28.8	1.8	2.5	29	1.69	1.1	2.04	0.7	28	2.46	2.69	28.5	-0.2	3.28						
110	5.5	32.7	1.25	4.7	30.8	1.69	4.5	32.3	27.5	1.98	2.5	27.7	1.89	1.2	2.05	0.8	28.3	2.48	2.69	28.6	-0.2	3.28	-0.4	27	2.39	-0.6	21.8	4.79
115				4.7	32.2	1.8	4.6	32.4	28	2.42	2.5	31.8	2.37	1.4	2.13	0.8	28.4	2.5	2.69	29.2	-0.2	3.27	-0.4		2.43			
120	5.8	35.1	1.4	4.7	35.8	1.9	4.5	38.8	33.6	3.38	2.5	37	2.95	1.4	2.88	0.8	28.3	3.35	2.71	30	-0.2	3.27	-0.4	26.3	2.46	-0.5	21.7	4.76
125			2.02	4.6	46.2		4.3	40.2	35.6	5.45	2.5	29	4.86	1.3	4.36	0.7	28	4.43	3.11	29.7	-0.2	3.27	-0.4		2.45			
130							3.8			8.21	2.2	24.9	5.69	1.2	4.65	0.7	30.7	4.75	4.02	29.7	-0.2	3.27	-0.4	26.2	2.43	-0.5	21.3	4.75
135										9.33						0.6	31.4		5.31	29.6	-0.2	3.27	-0.4	26.1	2.42			
140																				30.1	-0.2	3.37	-0.4	26	2.45	-0.4	21.3	4.73
145																					-0.3	4.33	-0.4	25.9	2.45	-0.4	21.1	4.72
150																							-0.4	25.8	2.41	-0.4	21	4.71
155																								25.5		-0.4	20.2	4.71
160																										-0.4	15.5	4.72

* DO was collected the following day on the 27/02/08

Appendix 4: Model Input Data

Table A4.1 Input data to FREZCHEM62 under a freezing regime for MIS meltwater ponds.

Input Requirements	Unit	Upper Pond 05 (F)	Upper Pond 07 (F)	Huey Pond 05 (F)	Huey Pond 07 (F)	P70 Pond 05 (F)	P70 Pond 07 (F)	P70E Pond 05 (F)	P70E Pond 05 (F)	VXE6 Pond 07 (F)	Orange Pond 07 (F)	P70 Pond 08 (F)	Orange Pond 08 (F)	Egg(timer) Pond 08 (F)	Skua Pond 08 (F)
Freeze (1) or Evaporation (2)		1	1	1	1	1	1	1	1	1	1	1	1	1	1
Equilibrium (1) or Fractional Crystallisation (2)		1	1	1	1	1	1	1	1	1	1	1	1	1	1
Na	mol/L	0.10258	0.057975	0.058332	0.040081	0.037653	0.044995	0.046267	0.049337	0.058508	0.129365	0.053944	0.033196	0.006543	0.059433
K	mol/L	0.001382	0.00093	0.001277	0.001054	0.000879	0.001051	0.000985	0.001125	0.001342	0.003131	0.001453	0.000954	0.000156	0.001076
Ca	mol/L	0.000646	0.000441	0.001033	0.000972	0.00086	0.001054	0.004679	0.005461	0.003946	0.001643	0.001355	0.000205	8.12E-05	0.001805
Mg	mol/L	0.002689	0.001566	0.006939	0.00413	0.004644	0.004397	0.009805	0.009172	0.008367	0.007454	0.00474	0.002034	0.00116	0.004239
Cl	mol/L	0.065083	0.037392	0.060174	0.043684	0.04082	0.048143	0.070202	0.067778	0.056626	0.108316	0.058502	0.030255	0.007674	0.030254
SO_4	mol/L	0.016629	0.009677	0.003345	0.002067	0.002065	0.002627	0.001858	0.001748	0.006769	0.00711	0.003315	0.001645	0.000279	0.018015
NO_3		0	0	0	0	0	0	0	0	0	0	0	0	0	0
HCO_3	mol/L	0.006838	0.005073	0.002472	0.001393	0.002265	0.001971	0.001061	0.001533	0.001641	0.021952	0.001324	0.002893	0.000812	0.013163
pH		9.8	9.7	9.4	10.1	9.4	9.7	8.8	9.7	9.5	9.7	10.4	9.7	9.6	9.7
CO_2(atm)	bars	0.00035	0.00035	0.00035	0.00035	0.00035	0.00035	0.00035	0.00035	0.00035	0.00035	0.00035	0.00035	0.00035	0.00035
acidity		0	0	0	0	0	0	0	0	0	0	0	0	0	0
start temp	K	278.15	278.15	278.15	278.15	278.15	278.15	278.15	278.15	278.15	278.15	278.15	278.15	278.15	278.15
end temp	K	248.15	248.15	248.15	248.15	248.15	248.15	248.15	248.15	248.15	248.15	248.15	248.15	248.15	248.15
Temperature Increments	K	1	1	1	1	1	1	1	1	1	1	1	1	1	1

Table A4.2 Input data to FREZCHEM62 under an evaporation regime (E) for MIS meltwater ponds.

Input Requirements	Unit	Upper Pond 05 (E)	Upper Pond 07 (E)	Huey Pond 05 (E)	Huey Pond 07 (E)	P70 Pond 05 (E)	P70 Pond 07 (E)	P70E Pond 05 (E)	P70E Pond 05 (E)	VXE6 Pond 07 (E)	Orange Pond 07 (E)	P70 Pond 08 (E)	Orange Pond 08 (E)	Egg(timer) Pond 08 (E)	Skua Pond 08 (E)
Freeze (1) or Evaporation (2)		2	2	2	2	2	2	2	2	2	2	2	2	2	2
Equilibrium (1) or Fractional crystallisation (2)		1	1	1	1	1	1	1	1	1	1	1	1	1	1
Na	mol/L	0.10258	0.057975	0.058332	0.040081	0.037653	0.044995	0.046267	0.049337	0.058508	0.129365	0.046212	0.032236	0.043564	0.010595
K	mol/L	0.001382	0.00093	0.001277	0.001054	0.000879	0.001051	0.000985	0.001125	0.001342	0.003131	0.001242	0.000927	0.001008	0.000221
Ca	mol/L	0.000646	0.000441	0.001033	0.000972	0.00086	0.001054	0.004679	0.005461	0.003946	0.001643	0.001162	0.000206	0.000516	0.000328
Mg	mol/L	0.002689	0.001566	0.006939	0.00413	0.004644	0.004397	0.009805	0.009172	0.008367	0.007454	0.004066	0.002029	0.007375	0.000721
Cl	mol/L	0.065083	0.037392	0.060174	0.043684	0.04082	0.048143	0.070202	0.067778	0.056626	0.108316	0.049742	0.029284	0.048065	0.005432
SO_4	mol/L	0.016629	0.009677	0.003345	0.002067	0.002065	0.002627	0.001858	0.001748	0.006769	0.00711	0.002739	0.001593	0.001568	0.003261
NO_3	mol/L	0	0	0	0	0	0	0	0	0	0	0	0	0	0
HCO_3	mol/L	0.006838	0.005073	0.002472	0.001393	0.002265	0.001971	0.001061	0.001533	0.001641	0.021952	0.00113	0.002772	0.005438	0.00243
pH		9.8	9.7	9.4	10.1	9.4	9.7	8.8	9.7	9.5	9.7	10.4	9.7	9.6	9.7
CO_2(atm)	bars	0.00035	0.00035	0.00035	0.00035	0.00035	0.00035	0.00035	0.00035	0.00035	0.00035	0.00035	0.00035	0.00035	0.00035
acidity		0	0	0	0	0	0	0	0	0	0	0	0	0	0
Start Temperature	K	278.15	278.15	278.15	278.15	278.15	278.15	278.15	278.15	278.15	278.15	278.15	278.15	278.15	278.15
Start Water Volume	g	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
End Water Volume	g	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Water Increments	g	10	10	10	10	10	10	10	10	10	10	10	10	10	10